

2.2.2. Past, present and future exposures from natural elements

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1. Is a million-fold enhancement of natural element mobilisation a problem?

1.1 Unprecedented scale of mining

Anthropogenic material turnover via mining and other extraction from the earth's crust is a prerequisite for modern society and its agriculture, building, transportation and other endeavours. For about one-third of all elements, the scale is larger than that of natural processes such as weathering and volcanic eruptions. For rare elements like osmium (Os) and iridium (Ir), anthropogenic mobilization may be more than a million times the natural mobilization (UNEP 2013). For some elements, resources are even transferred on a large scale from ores to in-stock and waste deposits (Rauch 2012).

This mobilisation upsets natural balances and may for instance lead to depletion of natural resources, climate change and toxic effects on humans and environmental organisms. With respect to the latter, environmental levels of lead and mercury have been associated with effects on the central nervous system that may impact on intelligence or behaviour (Simeonov *et al.* 2011), and relatively large areas in Poland, Ukraine and Russia are at risk of losing 1 per cent of their environmental species due to contamination with cadmium and lead (UNEP, 2013). There are thus problems associated with this large-scale mobilisation. Elucidating them might benefit from a systematic elaboration across the whole periodic system of elements. This is a formidable task and any review needs to clearly limit the chosen topics.

1.2 The scope: overview of exposures of humans and soils

Some attempts have been made to provide an overview of how natural elements are extracted and how this impacts on the environment and human health (Kabata-Pendias and Mukherjee 2007, Smith and Huyck 1999). Natural exposures of humans via the diet may be enhanced because of food additives and contaminated soils, and further enhancement may result from amendment of soils with sewage sludge. While there are many reviews of exposures, none are known to the author that provide a unified view of exposure enhancements.

The footprint of global production of elements can be found in different media with different sensitivities.

- It is most sensitively traced in media where a relatively narrow time-period can be defined. Air contamination provides a very immediate testimony to industrial activities, and different elements have been locally linked with different industries (Querol *et al.* 2007).
- Depositions integrated over the time scale of years have led to maximum enhancements of 140 times for Tibetan ice (cadmium, Grigholm *et al.* 2016), 250 times for Swiss peat (cadmium, Shotyk and Krachler 2004), 1000 times for Canadian snow (cadmium, Shotyk *et al.* 2010), and 1000 times for Swedish lake sediments (lead, Renberg *et al.* 2002).

- When time averaging occurs in a century scale such as for agricultural soils (Bengtsson 2015), enhancement rates become lower. Local high concentrations of Cd, Cu, Hg, Pb and Zn can be linked with human activities, i.e. urbanization, industrialization and intensive agriculture (Rodriguez Lado *et al.* 2008) while broad-scale contamination is more difficult to demonstrate.
- Sewage sludge belongs to the media that reveal enhancements relatively rapidly. For instance, platinum group element abundances in stored incinerator ash of varying ages appear to have been affected by the variation in use of Pt, Pd and Rh in catalytic converters due to variation in their market prices (Jackson *et al.* 2010)

Some details are given below about the natural elemental metabolism with respect to humans and its enhancement through anthropogenic mobilization of elements. The approach is empirical, looking at ways of systematising available data. Because of the overview character, only average exposures over large population groups or geographical areas are considered. Special critical groups or hotspots in limited regions might have exposures that are ten- or even hundredfold the average exposures, but the current focus is on broad averages.

1.3 Objectives

The purpose of the present review is to give a broad perspective on human and some environmental exposures stemming from the extraction of elements from the earth's crust. Contributions from anthropogenic use of the elements could then be seen in the light of the unavoidable contributions from human living on earth.

More specifically, the current paper sets out to

- give a generalised model for normal human intake of elements from the earth's crust
- illustrate how natural levels of elements in European topsoil and sewage sludge have been amended by contributions due to human activities
- relate the enhanced elemental content in topsoil and sewage sludge to production of the elements and to fossil fuel combustion
- forecast how the elemental content in topsoil and sewage sludge will develop in broad terms over the next human generation.

Because of the many generalisations and simplifications, the results are expected to be useful to generate hypotheses about the exposures rather than giving good descriptions. Such hypotheses could for instance be useful in setting priorities for further research.

The risks to health and the environment from enhanced elemental contents are outside of the scope of the current presentation, but some indications about such risks will be given.

2. Method

The presentation deals with exposures due to elements extracted from the earth's crust. Much of the discussion concerns elements in sewage sludge. The sludge component of naturally occurring elements basically follows the pathway: extraction from the earth's crust → emissions during the element's life cycle → water, soil, air, plants, animals → human intake → excretion → wastewater → sewage sludge. A significant component bypasses the human intake and forms a separate stream built on

- household and commercial use of elements, from which wastewater is collected, often including significant bulk components that will be turned into sludge,
- runoff collected above all in densely populated areas; the elements are only associated with a small bulk component that will be transformed into sludge, and they come from
 - depositions after transport via air and water, or from
 - emissions from human activities or infrastructure, such as use of cars or corrosion from buildings.

Elements from these chains are dealt with from four different angles:

- Normal human intake and its links to element levels in plants and in pore water of agricultural soils
- Enhanced levels in European soils
- Enhanced levels in sewage sludge
- Trends for the future.

For each of these, existing data were reviewed using the methods described in turn below.

2.1 Normal human intake

The objectives of this part of the review were to find the normal human intake

- to find transfer factors from topsoil concentrations to dietary intakes
- to establish a background level of excretion to sewage sludge
- for all selected elements in the periodic system of elements
- disregarding contributions from elements extracted from the earth's crust by man.

Dietary studies can give data on normal human intakes for many but not all elements. The results of the studies may be quite variable. The confidence in the obtained results needs to be increased, and intakes need to be extrapolated to elements for which no dietary studies are

available. A way forward could build on the realization that elements flow in biogeochemical cycles (Galloway *et al.* 2014). The concentrations in the earth's upper crust are on the whole mirrored in soil and water, with the exceptions discussed below in section 2.1.5. Organisms in food chains use the elements available in soil and water for their development and growth. It was hypothesized that the overall transfer of elements to humans might depend in rather general terms on the mean concentration of the corresponding element in the topsoil, combined with some rather simple chemical properties. The relevant transfer factor might then be the mean dietary intake of an element over large population groups divided by the mean concentration of the corresponding element in the topsoil. This quantity is in the following called the diet/soil ratio as a shorthand denotation.

To test the hypothesis of a systematic way to calculate transfer factors, data would need to be gathered on the following parameters:

- relevant elements
- the topsoil composition for these elements
- potentially important chemical properties of the elements
- mean human dietary intakes over large population groups for the elements

The acquisition of these data is described in the following.

2.1.1 Selection of relevant elements for the human diet

The following elements were deselected in the initial analysis:

- gaseous elements: noble gases, hydrogen, nitrogen, oxygen, fluorine, chlorine
- elements having no stable isotopes: technetium, promethium, astatine, francium, actinium, protactinium, transuranic elements (excepting uranium and thorium which are considered almost stable, having existed since the creation of the earth, and radium 226 and polonium 210 being relatively long-lived decay products of uranium)

Consideration was given to deselection of elements having potential to become liquid under natural conditions such as mercury (melting point $-39\text{ }^{\circ}\text{C}$), bromine (-7), cesium (29), gallium (30), and rubidium (39). No correlation could however be found between human intake and element melting points, so in the end these elements were included in the analysis.

Macroelements (aluminium, carbon, calcium, iron, potassium, magnesium, sodium, phosphorus, sulfur and silicon) are judged to be less interesting in the analysis of enhanced sludge contents. This is because the sludge does not represent incoming water; many of those elements are to a large extent released with the outgoing water, and others are added in-plant as part of the sewage plant process. While these were not included in the analysis of enhancement in sludge, they were used in the search for relations between chemical

parameters and dietary intakes.

Most of the macroelements were included in the measurement of enhancement of the element concentrations in topsoil. Since they are very common elements in soil with a concentration of about 1 % or more, the anthropogenic additions tend to be below the limit of statistical variability. The exceptions are P and S with a concentration less than 0.1 %; these are interesting for the topsoil enhancement analysis.

Some elements were deselected for analysis of human intake because of very special properties that were expected to make intakes fall outside of general patterns:

- period 2: Li, Be, B, C
 - Li does not have oxidation state -1 like the other alkalis and has extremely high second ionisation energy
 - Be is one of a few elements with negative electron affinity and has extremely high third ionisation energy
 - B has extremely high fourth ionisation energy
 - C has a complex interplay with i.a. the atmosphere and human agriculture, European topsoil has a typical carbon enhancement of about a factor of 25 above the earth's crust, based on European soil total organic carbon (FOREGS 2005).
- period 3: Na, Mg, Al, Si
 - Na has extremely high second ionisation energy
 - Mg is one of a few elements with negative electron affinity and has extremely high third ionisation energy
 - Al has extremely high fourth ionisation energy
 - SiO₂ is the most common constituent in soil making up 60 % of the earth's crust, and the dominance makes any fraction misleading

2.1.2 Potentially important chemical properties of the elements

There are numerous tabulations of properties of the periodic table elements and the relations of the diet/soil ratio to many properties were explored. Data that in the end were used for numerical relations encompassed the first, second and third ionisation energies retrieved from Wikipedia 2017. Tabulated values for ionisation energies are accurate to many decimals for all adequate sources.

2.1.3 Strategy to find data on the composition of topsoil

To find a system for transfer factors from soil element concentrations to dietary intakes, data are needed on the composition of topsoil. There are several difficulties in finding and such data. **First**, in principle, the topsoil only covers part of the pathway to the human diet. The dietary intake is not only derived from plants and animals living on the topsoil, but also from marine and freshwater organisms. However, seafood in a broad sense generally contributed less than a few per cent of the intake of elements in the large French dietary study (ANSES 2011) except for arsenic, mercury and silver. Further, as a mean across Europe, soil and sediment tend to have very nearly the same element concentration (FOREGS 2005), where the difference reaches a factor of 2 only for a handful of elements that does not include the three mentioned ones. Thus, the topsoil concentration should generally be a good indicator for the dietary intakes.

Second, there are significant difficulties in finding the required topsoil data.

- Very broad averages are available for Europe for 59 elements sampled near 1999 (FOREGS 2005) and the United States for 44 elements sampled about 1968 (Shacklette and Boerngen 1984) but these are predominantly not from agricultural areas while the dietary intakes mainly derive from agricultural soils. The soil concentrations may further contain a significant anthropogenic component that may vary with sampling time and soil depth.
- Very extensive European data are available from the LUCAS programme (Tóth *et al.* 2013) with emphasis on agricultural soils but these only cover 23 elements, were digested with aqua regia or microwave-assisted acid digestion that underestimates the total element concentration, and may contain the anthropogenic component.
- Also, extensive European data from agricultural topsoil are available for 26 elements from the GEMAS programme (Reimann 2013), giving total element concentration but still having the anthropogenic component.

Comparison of mean concentrations is possible for six elements (As, Co, Cr, Cu, Ni, Pb) surveyed in the FOREGS and LUCAS sets of data. The mean topsoil concentration from the LUCAS survey is 0.63 (range 0.38-0.79) of that from the FOREGS survey when aqua regia extraction was used in both surveys, and 0.47 (0.23-0.75) when the LUCAS aqua regia extracted values are compared the FOREGS total element values. Thus, the sampled agricultural topsoils have significantly less element concentrations than the general ones.

The totals of the GEMAS and FOREGS data can be compared for 26 elements. Here, the GEMAS agricultural soils on average had 1.11 times the concentration of the FOREGS general soils.

There is thus no clear-cut relation between topsoils in general and agricultural topsoils. Therefore, the FOREGS and US data were used for further analysis of potential transfer

factors from soil to diet. The selection of FOREGS data is discussed below under 2.3 Element concentrations in European topsoil.

Third, to find the natural human intake, anthropogenic contributions to the intake should be disregarded.

- One way of eliminating anthropogenic components is to look at the dietary intakes at different times and estimate intakes that might be free of anthropogenic component, as discussed in section 2.1.3.
- Another way is to find relations that enable elimination of such components from the topsoil element concentrations. While it is possible to distinguish anthropogenic components on a limited geographic scale (e.g. Querol *et al.* 2007), it is very difficult to find the anthropogenic component on a broader scale (Caritat *et al.* 2012). In the current review, a relation between human activities and topsoil concentrations was sought for major topsoil studies in the US (Shacklette and Boerngen 1984), Europe (FOREGS 2005 and Caritat *et al.* 2012) and Australia (Caritat *et al.* 2012). The uncertainties, however, were too large to enable identification of any such relation.
- A third way of finding possible anthropogenic topsoil components would be to look at the FOREGS topsoil/subsoil concentration ratios (section 2.3).

Finally, it would be very interesting to be able to predict an anthropogenic component. for elements for which there are no topsoil measurements. To this end, contributions from anthropogenic emissions to the topsoil were calculated and compared with topsoil concentrations (section 2.3).

2.1.4 Element concentrations in European soils and subsoils

For European soils, there is a large dataset available on i.a. topsoil and subsoil concentrations of many elements (FOREGS 2005). About 800 samples each of topsoil and subsoil have been systematically collected across Europe in 1998-2001. Two different depth related samples were taken at each site: a topsoil sample from 0-25 cm (excluding material from the organic layer where present), and a subsoil sample from a 25-cm thick section within a depth range of 50 to 200 cm. Areas with agricultural activities were avoided. The standard deviation among the samples for an element could amount to several times the mean value. However, because of the large number of samples, the standard error of the mean value across Europe would typically be in the percentage range.

No significant loss from the topsoil for newly added elements was expected. The mean penetration depth according to the penetration equation of Bengtsson (2015) was calculated to be 8-10 cm which is not sufficient to give any major loss from the top 25 cm of a soil, if there is little downward displacement of the metals due to soil management procedures. The parameter values used for calculating the penetration depth were

- the means found by FOREGS 2005, with values for subsoil in parenthesis, that is, pH

= 5.68 (6.01), and organic matter fraction 0.043 (0.0162),

- the sand fraction 0.17 taken from the LUCAS project (Ballabio *et al.* 2016), assumed to be the same for the subsoil
- a mean annual precipitation of 700 mm.

A small loss of the original elements in the soil might be expected as discussed by Bengtsson 2015. It should be noted that the findings of Bengtsson 2015 only comprised 10 metals that all mainly occur in positive oxidation states, and only were derived for agricultural soils.

2.1.5 Data on the composition of the earth's crust

Data on elemental abundance in the earth's crust were used to check the realism of the estimated topsoil abundance. Data are available for practically all elements and refer to total element concentrations. On the whole, the mean topsoil concentration of elements across the globe is near the earth's upper continental crust concentration, within about a factor of 2. There are, however, some notable exceptions (Goldschmidt 1937) where the soil concentration is enhanced up to a factor of 10 or more:

- the highly siderophile ("iron-loving") elements (Day *et al.* 2016) Ru, Rh, Pd and Re, Os, Ir, Pt, Au; the neighbour moderately siderophile elements Mo and W should be considerably less aberrant
- the chalcogen ("born from copper") elements in group 16 of the periodic system S, Se, Te (and the radioactive Po) and to a smaller extent their neighbour elements P, As, Br, Sb, I, Bi.

Crust data were mainly obtained from those recommended by Rudnick and Gao (2003). Most estimates of the major element composition of the upper continental crust fall within a 20 % standard deviation of the mean. Such an uncertainty also adheres to many trace elements, while very few estimates have been made of the upper crust's halogen, sulfur, germanium, arsenic, selenium, indium, and platinum-group element concentration (Rudnick and Gao 2003).

Rudnick and Gao 2003 do not provide data for some elements, or newer information is available, so the following additional sources were used

- For carbon, gallium and tellurium, the mean of the concentrations given by Barbalace, Web elements and Jefferson lab were used (Wikipedia 2018). The concentration of tellurium differs by a factor of 5 between the sources, that of carbon by a factor of 9. Carbon is already deselected.
- For ruthenium, rhodium, and platinum, the more recent data from Park *et al.* 2012 were used

2.1.6 *European topsoil concentration corrected with reference to the composition of the earth's crust*

The objective of this analysis was to increase the accuracy of the selected topsoil element concentrations, for elements for which there were ambiguous topsoil measurements. The basis would be the earth crust element concentrations which are available for all elements of interest for the current review, as detailed in section 2.1.5. The ratio of topsoil to crust concentration was studied. The ratio showed some variation with atomic number. This variation could be related to the siderophile and chalcophile aberrations and had a trend to increase with the geometric mean of the first three ionisation energies. There were two deviations from the general pattern

- the neighbour elements rhodium and palladium varied in ways that were not consistent with the other variations. It was assumed that this variation was due to uncertainties in both soil and crust concentration assessments. Soil concentrations for the two elements were adjusted to give the same soil/crust ratio. The adjusted concentrations were assumed to be better approximations to the real concentrations. A similar adjustment was made for tellurium and iodine.

2.1.7 *Mean human dietary intakes over large population groups for the elements*

Data were obtained on the mean dietary intake of adults (average of males and females) over larger regions in at least one country. The sources are detailed in the Appendix. A compilation of more than 200 dietary studies by Parr *et al.* 1992 was a good starting point.

Uncertainty within a factor of 3. Where data from more than one source were available, data from different sources were generally within a factor of 3 from the chosen value, except for lithium beryllium, chromium, arsenic, niobium, palladium, cadmium, tellurium, and mercury. The latter 8 elements were marked for uncertainty in some text and diagrams.

Lanthanides assessment. For lanthanides, one set of data was given by Ulusoy and Whitley (2000). Their ashweight contents were multiplied by 0.172 (Onabanjo *et al.* 2016) to give dry weight concentrations. The sum over all lanthanides corresponded to a daily intake of 34 µg, consistent with the mean daily intake of 36 µg (Zhuang 2017) from cereals for a control group. A power function was applied to describe the daily intake versus atomic number. Its power was 17 for the data of Ulusoy and Whitley (2000), consistent with the power of 18 describing the relations for pig liver and mushrooms (Zhang 2007). Soil concentration data were closely paralleling crust concentrations, with a ratio having a standard deviation of 9 %, and a power of 19 for the fitted power function. The data of Ulusoy and Whitley (2000) were used as the final choice for daily intake.

The chosen intakes overestimated some measured results from Canada (Health Canada 2007) for lanthanum and cerium by a factor of 4-7. Those studies only concerned one city at a time. The cerium result from Italy of Turconi *et al.* (2009) was underestimated by a factor of 5 by the chosen intakes, but their value was based on a very limited sampling, mainly referring to

cheese bought from one cafeteria. The global compilation on soil concentrations by Ramos *et al.* (2016) shows that a country like Denmark may have one-fifth of typical European soil concentrations, while five-fold higher concentrations are extremely rare, so the Canadian intakes may not be unreasonably low.

Checks if there was only one data source. The median number of sources for an element was 2, but for 7 elements no or one source of dietary intake was found: zirconium, hafnium, tantalum, tungsten, rhenium, osmium and iridium. In these cases, a proportionality analysis was made using available concentration data on

- plants, assuming a daily intake of 400 g dry matter
- human blood, assuming 20 % of all ingested elements pass the blood with a mean residence time of 5 days in 5 litres of blood
- human tissues, assuming 20 % of all ingested elements pass human tissue with a mean residence time of 100 days in 70 kg of tissue.
- intakes of other elements with similar chemical properties.

The major source for the proportionality analysis was Kabata Pendias and Mukherjee (2007). The 7 elements were marked for uncertainty in some text and diagrams. Additionally, smaller or special studies were used to check the proportionality of the result from the major study.

Heavier platinum group elements. There was very little information available for the platinum group elements. For the lighter elements Ru, Rh, and Pd, diet studies have been made in the United Kingdom (Rose *et al.* 2010) and the results are broadly consistent with those of the mentioned proportionality check. For the heavier platinum group elements Re, Os and Ir no data on intakes have been found. The UK total diet studies have tried to assess Ir intakes but concentrations in food have often been below the limit of detection (Committee On Toxicity 2008) and Ir intakes were later not reported among 30 elements (Rose *et al.* 2010). Neither have relevant plant uptakes been found. For Re and Ir therefore, only a very uncertain proportionality analysis is behind the current dietary intake estimates. Osmium between Re and Ir in the periodic system has an aberrantly low electron affinity and a fourth ionization energy that has no correspondence for Re and Ir, so interpolation may be a poor way to estimate a dietary intake. However, no other method seems to be available, so interpolation was still used. For 8 sewage plants in Sweden, detection limits in 2016 and some other years (Anders Finnson personal communication 2017) allowed inference that dietary intakes of Ru, Rh and Pd were 1 µg/day or less and those for Ir and Re 0.2 µg/day or less; for Pt fewer measurements also suggested 0.2 µg/day or less. These are not inconsistent with the final choices of 0.3-1 µg/day and 0.2-0.3 µg/day, respectively.

Deselecting anthropogenically enhanced intakes. The estimated transfer factors from soil to diet were based on soil concentrations including anthropogenic contributions. This is because the soil concentrations were mainly measured around the year 2000 and might have

persisted for decades, during which most of the dietary intakes had been measured. To find possible relations between soil concentrations and dietary intakes, this basis was judged the most relevant.

In contrast, the assessed basic dietary contributions to sewage sludge element concentrations were founded on intakes corrected for anthropogenic inputs. The latter can sometimes be very large. An extreme example refers to titanium, where a typical natural intake may be 300 µg/day, but present Dutch intakes are about 8000 µg/day due to amendments in candy, coffee creamer and other foodstuffs (Rompelberg *et al.* 2016). For the UK total diet study, there are data going back to 1976 (Committee on Toxicity 2008). They show significant decreases in the intakes of cadmium, chromium, lead, mercury, nickel and tin, suggesting that the earlier intakes had a significant anthropogenic component. In the current analysis pertaining to comparisons with sludge concentrations, care was taken to use as far as possible, for all elements, only data on intakes that would be free of anthropogenic enhancement. The dietary intakes were corrected with the soil enhancement factors derived under sections 3.2.1 and 3.2.2. Corrections below 20 % were neglected, meaning correction factors in the range 1.3 (Sb) – 1.8 (Hg) were only applied to the results for P, S, Cd, Sb, Hg and Pb. For the platinum group elements, no corrections were applied since there were very few measurement results available (compare section 4 about sludge concentrations).

For **scandium**, it was particularly difficult to find and evaluate dietary data due to the very large contributions to environmental levels from fossil fuel combustion mentioned under section 3.3.1. Parr *et al.* (1992) report means from 11 studies published in 1977-1992, centered around 0.35 µg/d and with a range 0.11-2.2 µg/d. Data for plants, e.g. in Kabata-Pendias and Mukherjee (2007), translated to daily intakes via ingestion of 0.4 kg/d, suggested much higher intakes, consistent with anthropogenic enhancement. Along similar lines, lung tissue had higher scandium concentrations than heart tissue. The final selection was 0.35 µg/d.

Final judgment on dietary intakes. A final judgment was used to establish dietary intakes that seemed reasonable in the light of available data including considerations of sewage sludge, urine and feces, time trends, consistency between data sets, size of the population involved, and other factors that might influence the choice.

2.1.8 Establishing the sludge contribution of normal dietary intakes

The minimal level of elements in sewage sludge derives from natural human intakes excreted via feces and urine. The normal production of feces and urine for an adult is about 35 g dry matter per day (Rose *et al.* 2016, Almqvist *et al.* 2007). Other contributions such as toilet paper and industrial sludge add about the same amount of dry matter (Almqvist *et al.* 2007, Statistics Sweden 2016), so the total amount of sludge is here assumed to be 70 g per person per day. This is consistent with the annual amount of sludge in Germany of 2 million Mg dry weight (Krüger and Adam 2014) which translates to 68 g per person per day.

The mean dietary intakes of the selected elements were derived according to section 2.1.7.

The associated dry matter concentration in sewage sludge was obtained by dividing the daily intake by 70 g of dry matter.

2.2 Anthropogenic emissions

Anthropogenic emissions were investigated to find possible links to element concentrations in soil and sewage sludge. The hypothesis was that similar emission patterns would apply for many elements. The patterns found for a few well studied elements could then enable estimation of emissions for elements for which the emissions have been poorly studied, and for instance guide priority setting for further study. Four parameters need to be studied:

- The mass of an element consumed in a country, or the mass of an element in the consumed fossil fuels.
- A relevant time period for use of the element
- The emitted amounts or the fraction of the used mass emitted to air over this time-period. The dimensionless emitted fraction is defined as the mass of an element emitted to air in a region divided by the mass of this element in the combusted fuel or in the mass of element from production, fabrication and use in this region.
- The geographical extent of the deposition resulting from the emissions.

In the following, these are discussed. Thereafter, a proportionality check is performed for the resulting emissions. It should be noted that the approach is highly simplified. Production of one element such as copper may lead to significant emissions of another such as arsenic, as evident from listed emission factors (USEPA 1973). The simplifications inevitably will lead to large variations in the results of the analysis.

2.2.1 The mobilised element mass in consumption and combustion

Consumption. For many elements, the main emissions nowadays come from the production of the elements themselves, and from the use and disposal of the products based on these elements. The global production mass should thus be an indicator of the emission potential for most elements. Data on the global production of elements were mainly obtained from the most recent compilations by the British and US geological surveys. Historical data were obtained from USGS (2018). Where data on smelter production were available, these were preferred over mine ore production since scrap metal smelting and use would also contribute to emissions. For a small number of elements, production data were obtained from other sources. Production rates typically vary between years by 10 % to 30 %, so this is the minimum uncertainty adhering to the estimates for any chosen year. Adjustment to other regions and years was made using the gross domestic products, as described in section 2.4.5. It has been shown that material extraction increases with the gross domestic product as exemplified with the case of aluminium (OECD 2011, OECD 2015). The smaller the gross domestic product is, the larger will the uncertainties be in this adjustment. Detailed assessments for *sewage sludge* were made for Sweden with 0.8 % of the global gross

domestic product and Germany with 7 %. A very large spread made the assessments for Sweden little useful, so in the end the assessment of anthropogenic components was only reported for Germany. For *soils*, the assessments were made for the European scale which should be large enough to enable reasonably good estimates of production volumes.

Combustion of coal. For low production volume elements, the emissions from combustion and other uses of fossil fuel might still be significant, as shown by the thallium example in section 2.3.4 and the results in section 3.3.2. A very approximate assumption for the emission from fossil fuels can be derived from the contents of elements in coal multiplied by a factor for the emission to air, assuming that coal dominates the combustion emissions. The largest contribution to emissions from fossil fuels is generally due to burning of coal, although oil might give significant contributions for elements like nickel and vanadium (NYSERDA 2011). Elemental contents in coal were derived as estimated arithmetic averages for different coals given by Nalbandian (2012). Where data were lacking or Nalbandian (2012) only gave data from one region, the following sources were also used.:

- phosphorus, aluminium, sulfur, tin, hafnium: Orem and Finkelman (2005)
- iron: several publications gave a concentration of about 0.7 of that of aluminium
- lanthanides and yttrium: Kruger (2017). Testing of coals from North Dakota in the USA show very close agreement between the contents of lanthanides in the upper continental crust and in coal. The concentrations for cerium and tantalum are similar to those of Akinyeye *et al.* 2016.
- bromine: Schweinfurth (2009)
- ruthenium, rhodium, palladium, iridium, platinum: Dai *et al.* (2003)
- iodine: Wang *et al.* (2005)
- thallium: Lopez Anton *et al.* (2013)
- tellurium: Bullock *et al.* (2017) who also review higher abundances in some environments; Oda and Arikawa (2005).

It should be noted that these values are very approximate for Germany, where a large share of the coal use comes from lignite. Several trace elements may have much higher concentrations in lignite than the ones used in the calculations.

Combustion of petroleum products. For the analysis of enhanced element levels in sewage sludge (sections 2.4 and 3.3), sludge data sets from Germany and Sweden were tested. For Sweden, however, there was a strong component of petroleum products that was confounding the analysis and contributed to deselecting the assessment for Sweden.

For gasoline and diesel, the element concentrations are all in the range of a fraction of a milligram per kilogram (Pulles *et al.* 2012, Kitto 1993) and thus much smaller than those of

coal. The same holds for lighter fuel oils (Graham 2010, Kitto 1993). Considering the uncertainties in the current review, the emissions from gasoline, diesel, and lighter fuel oils could thus be neglected. For the heavier residual oil, concentrations might be similar to those of coal. The accounting for this oil is described in section 2.4.5. In the case of Germany, fossil fuels were dominated by coal, so this was the major fossil fuel accounted for, with a smaller correction for residual oil.

2.2.2 The relevant time periods of use

It was recognized that emissions affecting soils had occurred over a much longer time period than emissions affecting sewage sludge, and with different emitted fractions of the involved elements. Concentrations in sewage sludge should mainly reflect recent emissions. Concentrations in topsoil should for many elements represent integration over decades (Bengtsson 2015).

For derivation of additions to soil concentrations of the elements, the cumulative air emission in Europe is required. Data are easily available for the period 1990-2015 (Eurostat 2017). For the years before 1990, limited estimates are available.

- For the UK, data from Vincent and Passant 2006 indicate that emissions between 1970 and 1990 were the following in relation to the emissions 1990-2015, arsenic 2.1; cadmium 2.7; nickel 3.2; and lead 7.9,
- Emissions before 1970 have been discussed by Nriagu (1996). For copper, lead and zinc, the emissions between the years 1900 and 1970 were estimated at about 0.9; 1.5; and 1.3, respectively, of the emissions between 1970 and 1990.
- Mylona (1996) provides detailed estimates of sulfur dioxide emissions in the period 1880-1991. This translates to cumulative emissions corresponding to about 80 times the emissions in 1999.
- Trace elements have been measured in two peat cores from Belgium (Allan *et al.* 2013). Records of Cu, Ni, V, Cr, Co, and Sb suggest significantly raised depositions from about 1850, corresponding to cumulative emissions of about a century at the intensity from 1999. The time span is longer and more diffuse for elements like Zn, Pb, As and Cd. One of the cores has a clear superposition of a component from exploitation of a nearby ore from the Roman Empire to 1945.

The final choice was to assume a single emitted fraction across the years and elements. This entailed assessment of accumulated combustion and consumption. For coal in the European FOREGS countries, the consumption in 1999 was 508 Tg and the assumed cumulative consumption 50800 Tg corresponding to 100 years at the 1999 level, as calculated based on Mylona (1996). For consumption, the USGS data (2018) on world production were used to calculate the number of years of consumption in Europe equivalent to that of 1999. This number ranged from 12 years for Pd and 15 for Rh to 60 for tin and exceptionally 400 for Hg,

demonstrating the large reduction of mercury consumption in recent years.

2.2.3 The emitted fractions decreased in recent years and depend on element boiling point

Recent emitted fractions are lower. After the increase in anthropogenic mobilization of elements about a century ago, large emissions occurred from materials use, such as production of elements, burning of fossil fuel, or corrosion from copper roofs. With increasing end-of-pipe emission reductions in the latter half of the twentieth century, the importance of the corresponding emissions has decreased. In the year 2000, besides emissions from natural sources, emissions above all to air had strong contributions from the combustion of fossil fuel and from production, fabrication, use and discarding management of elements (Rauch and Pacyna 2009). The relative contributions of production and combustion varied in the approximate range 0.1-10 for 8 elements studied in detail by Rauch and Pacyna (2009), with small production shares for aluminum, iron and lead. The ongoing emission reductions mean that emissions around the year 2014 are much lower than those that occurred during the 20th century. The emission reductions can be illustrated by sulfur dioxide emissions which in 1880 amounted to 5 Tg, had a peak of 57 Tg in 1975 (sulfur dioxides, Mylona 1996) and were then reduced to 25 Tg in 1990 and 3 Tg in 2015 (the latter pertaining to sulfur oxides for a somewhat different selection of countries, Eurostat 2017). Mylona (1996) discusses sulfur retention in the ash from hard coal combustion as being 20 % around the year 1900, going down to 5 % a century later as a result of higher combustion temperatures, and correspondingly 45 % to 25 % for brown coal. She also discusses how sulfur dioxide emissions for production of copper went down from 2,5 Mg SO₂ per Mg copper metal to 0.01 in the eighties, for lead from 0.7 to 0.1 Mg SO₂ per Mg lead metal and for zinc from 1.1 Mg SO₂ per Mg zinc metal to negligible levels. For the current discussion of emissions in coal combustion influencing soil element concentrations, it seems likely that the overall cumulative emitted fraction for sulfur has been about 0.8.

Emitted fractions depend on time and boiling point power. Emission factors depend in complicated ways on elements chemistry and application technology. For 11 elements dealt with in USEPA involving public energy works (1995), the emitted fractions varied from about 1 % (lead, cobalt, nickel, beryllium, chromium, antimony) to about 30 % (selenium, mercury, cadmium), with arsenic inbetween. The USEPA emitted fractions seem to depend approximately on the inverse square of the boiling point of the element. The utility of a temperature dependence for the emissions factors was tested, both for boiling point and melting point. The results were less variable when boiling point was used, so use of the melting point was not further pursued. Apparently, the boiling point dependence increased over the years. This is consistent with stronger emission reductions which are easier to apply to element with high boiling points.

A more precise dependence than the inverse square of the boiling point of the EPA emitted fractions was obtained for the emitted fractions in the year 2014 for 8 elements from four European regions: Germany, Sweden, the United Kingdom and the countries participating in the FOREGS assessment (2005) of element concentrations in soil. Countries report

emissions to air of up to 9 elements (Cr, Ni, Cu, Zn, As, Se, Cd, Hg, and Pb) to EMEP (2018) under the UNECE Convention on Long-range Transboundary Air Pollution. The ratio of the emitted mass of an element and the mobilised element mass was studied for 8 elements reported to EMEP. Selenium which was also among the reported elements was excluded since broad data were not available for its concentration in coal. The emitted mass was retrieved from the EMEP database (EMEP 2018). The mobilised element mass was derived as described in sections 2.2.1-2.2.2 above.

There was relatively little variation between the chosen 4 geographical regions (typical geometric standard deviation about 1.5 between regions for an element). The geometrical mean emission for an element of the 4 regions depends approximately as a power function on the element's boiling point. The coefficient of determination R^2 is typically around 0.7 and the power ranges from -2 to -3.

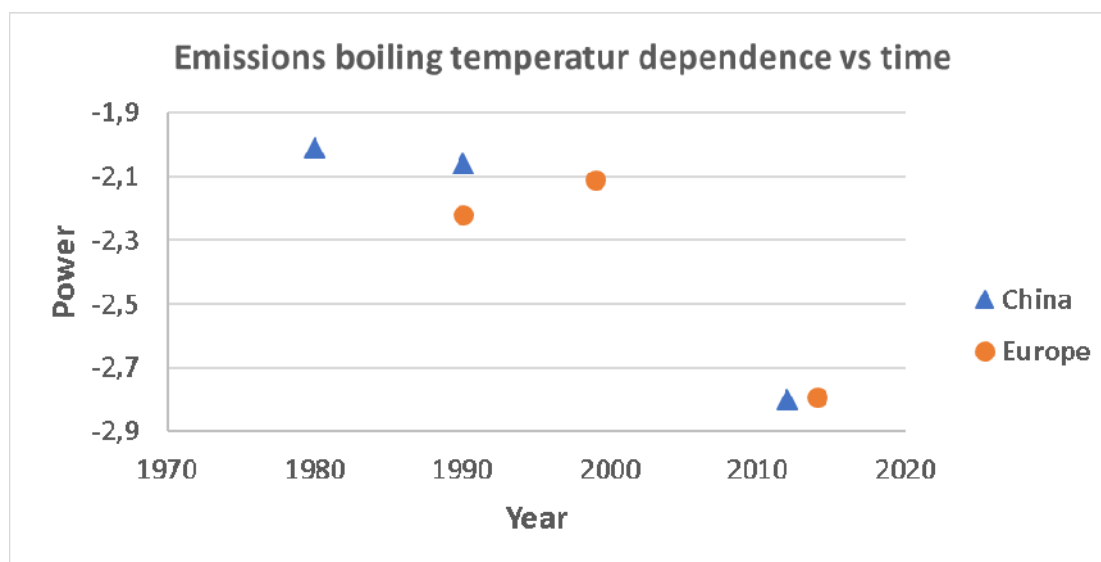


Figure 1 Boiling point dependence of emitted fractions as a function of time. The emitted fractions depend approximately as the power of the boiling point of the different elements. The powers determined for Europe were based on EMEP (2018) and pertained to 8 elements; those for China were derived from Tian *et al.* (2015) and were based on 12 elements. In recent years the boiling point dependence is stronger.

The reported emissions are subject to large uncertainties. It had been noted in 2003 (UNECE 2003) that while there had been much progress in recent years on reporting heavy metal emissions, such emissions were probably significantly underestimated. Similarly, it had also been observed for cadmium and lead that official reported emissions estimates in modelling in the EMEP region have resulted in significant (2-3 times) underestimation compared to measurements (EMEP 2007). However, the relation of emitted fractions between elements may be less uncertain and were used for estimates of the boiling point dependence of the emitted fractions.

Similar analyses were made for the 15 countries of the European Union in 1990 and 1999,

and for emissions in China in 1980, 1990 and 2012 reported by Tian *et al.* 2015. The power of the fitted power functions seemed to depend on time, with a stronger temperature dependence in recent years, as given in figure 1. It should be noted that the two sources behind figure 1 (mobilised element mass and element mass emitted to air) both comprise the aggregated result of a multitude of sources and combustion as well as emission reduction techniques. Emission data for single sources and techniques (USEPA 1995, EEA 2017) do not give similar clear trends with boiling point.

When a boiling point dependence was applied to emissions affecting the concentration of elements in European soil, no clear-cut decrease in variation between elements was obtained. In the end, therefore no temperature dependence was applied to the emissions. This is reasonable in view of the long period of very limited emission reduction measures when depositions were integrated in the soil. For emissions affecting sewage sludge, much shorter time periods should be relevant. For recent emissions, recent boiling point dependencies might be applied, but they failed to help reducing uncertainties in attributing sources to German sludge (section 3.3.2).

2.2.4 Spatial extent of deposition

Detailed accounts have been made for a few elements such as lead, cadmium and mercury (EMEP 2016) showing that local emissions and associated depositions may vary more than thousand-fold across Europe. The distances involved may exceed 100 km for non-ferrous smelters (Ettler 2016) and coal burning power stations (Chemel *et al.* 2011) but are still small compared with the extent of most European countries. Emissions in Europe would then mainly be deposited in Europe, excepting elements with low boiling points which are emitted to air to a larger extent than those with higher boiling points. The most obvious example is elemental mercury which tends to disperse long distances and may not deposit until it has travelled hundreds or thousands of kilometers (Sundseth *et al.* 2017). Other elements with similarly low boiling points might also be more widely dispersed: P, S, As, Se, Br, I, Cs.

The assessments made in the following pertain to average enhancements of elements in sewage sludge in Germany, and in soils in Europe. In both cases, it should be a good approximation that the emitted elements are also deposited in Germany and Europe, respectively, except for mercury and possibly a few other elements.

2.2.5 Measured emitted fractions used for proportionality check of the selected emitted fractions

The ensuing assessments for excess concentrations in both soil and sewage sludge used a single emitted fraction from coal combustion and another from element consumption. The time period for the soil excess involved a cumulation until 1999, while the assumed relevant time period for the sewage sludge excess was the year of sludge collection, that is 2011.

Extensive compilations of default emission factors for combustion exist for North America (USEPA 2018) and Europe (EEA 2017). Data on default emitted fractions were typically

collected in the period 1990-2005. The emission data from EMEP (2018) indicate that the emitted fraction for lead in 2014 was about one-tenth of that of 1990, and that of other elements typically one-half, consistent with the general decrease in emitted fractions with time which has prevailed since the 1970's. The default data therefore are neither ideal for the soil excess assessment period 1900-1990 nor for the sludge relevant period around 2011. For the former, it is difficult to find alternative emitted fraction data since broad-scale emission data have only been reported after 1990. For the sludge relevant time period after the year 2000, there is scarce information. The emissions factor databases of EMEP/EEA (EEA 2017) and USEPA (2018) mainly give data from before 2008. Mylona (1996) gives a few examples mentioned in section 2.2.3. Some other examples are

- A very extensive discussion of best available techniques has been published within the European Union (Lecomte *et al.* 2017). Mass balances suggest that for most metals and metalloids, a fraction below 0.001 reaches the flue gas from the stack with mercury as the exception with an emitted fraction of 0.3.
- Reported emissions to air for Europe in 2014 (EMEP 2018) for Cr, Ni, Cu, Zn, As, Cd and Pb correspond to emitted fractions of 0.0002-0.014 in relation to consumed element mass. Hg is an exception with a fraction 0.09. Early reported emissions have been considered underestimates, as discussed in section 2.2.3.
- The largest modern emitted fraction for copper production is less than 0.0001 (EEA 2016). However, the emission of copper from brake wear in Europe in the year 2000 has been estimated to 2,4 Gg/a (Hulskotte *et al.* 2007) and the total copper emission to 5 Gg. With an annual European copper production of about 4000 Gg, the total emitted fraction would be about 0.001.
- Copper concentrations have been measured in peat at background sites in the UK (Livett *et al.* 1979) and Belgium (Allan *et al.* 2013). The general trend was very approximately constant deposition since the beginning of the 20th century and annual deposition rates of about 0.4 – 4 mg/m². Within this range, a rate of 1 mg/m² was found for forests in Sweden and Germany (referenced in Reinds *et al.* 1995). At the FOREGS soil mass of 300 kg/m², for deposition over a century, this corresponds to a topsoil/subsoil increase of about 0.8 % to 8 % which is not inconsistent with the observed, not significant, increase of 4 %.
- For a large range of elements the calculated mean fraction of the consumed amount recovered in sewage sludge in Germany in 2011 was 0.0026 (section 3.3.2).
- A detailed analysis of metal flows in Stockholm, Sweden, was made by Månsson *et al.* (2009), for lead, cadmium and mercury. Their total supply for the year 2000 was respectively 1 times, 0.5 times, and 0.1 times the supply derived by scaling the global supply with the gross domestic product of Stockholm in relation to the global one. The low supply for cadmium and mercury might reflect Swedish efforts at reducing their use. The emissions calculated by Månsson *et al.* 2009 did only account for gasoline among

fossil fuels and not the larger contributions from coal and oil. There were many unknown emissions, for instance for mercury sewage pipes, electronics and thermometers

- The sludge in Stockholm (Länsstyrelsen i Stockholms län 2014) in the year 2000 contained 3 %, 30 %, and 1700 % of the mentioned total supply that year for lead, cadmium and mercury, respectively. The high contribution from mercury might reflect the unknowns, the high volatility of mercury, and depositions originating outside of Stockholm, consistent with the significant long-distance dispersion of previously deposited mercury highlighted in section 2.2.4.
- The German emission reports (EMEP 2018) give total emissions of chromium, nickel, copper, zinc, arsenic, selenium, cadmium and lead. The fraction of the air emitted element mass recovered in sewage sludge ranges from 0.07 (Hg) to 4.3 (Ni) with a geometric mean of 0.8 and the highest fraction being 60 times the lowest one. Only 9 % of the emitted mercury is accounted for in sludge. The German data for mercury have some peculiarities: mercury was only measured in 143 samples while most other elements were measured in 252 samples; the variability of measured ash concentrations among installations was higher for mercury than for all other element in trace element group 4; and mercury is extremely enriched in the flue gas cleaning gypsum. Coupled with the volatility of mercury and the mentioned long-distance dispersion, these facts suggest that a further analysis is required to account for the low mercury recovery in sludge ash.
- The corresponding Swedish data on sludge for the year 2000 are more accurate than the German ones, with weighting of the total mass of elements according to the volumes treated at each sewage plant. They also include data for Se. The fraction of the air emitted element mass recovered in sewage sludge ranges from 0.25 (Ni) to 2.1 (Cu) with a geometric mean of 0.7 and the highest fraction being 8 times the lowest one, thus a considerably narrower range than for German emissions and sludge.

Very broadly, thus, emitted fractions in 2011 should be about 0.001 to 0.01 with mercury, selenium and maybe a couple of other elements reaching 0.1. For many elements (Ni, As, Zn, and for Sweden also Cu), more mass is recovered in sludge than was emitted to air. This shows that for some elements, other pathways to sludge than via air emissions may be important.

2.3 Possible anthropogenic enhancement of average European topsoils

The objective of this analysis is to find if elemental concentrations are enhanced in European topsoil, and if so, whether there is a relation to European emissions that can be used to generate hypotheses about enhancement of elements in general.

2.3.1 Topsoil enhancement versus ionisation energy

An extensive data set is available for European soils (section 2.1.4), including topsoil and subsoil concentrations of many elements (FOREGS 2005). Since there is a strong correlation

between topsoil and subsoil concentrations their ratio as an average across Europe would be quite accurate. A typical relative standard deviation topsoil/subsoil among sites would be about 30 %. The standard error of the mean value of about 800 samples would then be about one or two per cent. This is approximately consistent with the variation of the topsoil/subsoil ratio for elements with low global production rates, as shown in the next paragraphs.

For normal human intakes of elements, it turned out that the element's ionisation energy may be an important parameter. The utility of this parameter was explored also for the topsoil/subsoil ratio. A rationale was that plant uptakes are related to the ionisation energy. Hypothetically, these might be more significant in topsoil than in subsoil and then the topsoil/subsoil element concentration ratio might depend on the ionisation energy. From the FOREGS data set, for each of the available 54 elements, the mean concentration T across the topsoil samples was divided by the mean subsoil concentration S . This ratio T/S was plotted against the geometric mean i of the first three ionisation energies of the elements. To account for possible anthropogenic components in the topsoil/subsoil ratio, the elements with the lowest combination of produced mass and mass used in coal relative to their content in topsoil were identified (Al, Ba, Ce, Co, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, La, Lu, Nd, Ni, Pr, Rb, Sc, Si, Sm, Sr, Tb, Th, Tl, Tm, U, V, Y, Yb). Their T/S ratio relation to the geometric mean of the first three ionisation energies fitted quite well a straight line with no ratio above 0.05, 21 ratios above 0 and 14 ratios below 0. The equation of the line was $T/S = 0,0068 * i + 0,86$, where i has the unit eV.

Elements with a T/S ratio above that given by the equation plus 0.05 are very likely to have a significant excess topsoil element concentration. These elements were selected for further analysis (Ag, Cd, Cr, Hf, Mn, Mo, Nb, P, Pb, Sb, Sn, Ti, Zn, Zr). The objective was to find any relation between air emissions of the elements and excess topsoil element concentration. Since it turned out that a clear relation of minimum ratio versus ionisation energy was found (previous paragraph), the same approach was applied to the ratio of stream sediment/subsoil concentration. The rationale was here that the stream sediment would to a large extent be derived from the uppermost topsoil layer and thus might be more sensitive to changes in the topsoil concentrations.

The relations found for minimum topsoil/subsoil and stream/subsoil concentration ratios versus ionisation energy were used to generate an excess topsoil/subsoil or stream sediment/topsoil concentration ratio X . This was obtained by subtracting the minimum ratio R_{\min} from the observed ratio R : $X = R - R_{\min}$. The thus obtained excess ratios were used to study the relation between emitted element mass and the observed excess mass of the element.

2.3.2 Assessment of leaching of deposited elements

For many elements, the excess ratio was not significantly different from the minimum ratio R_{\min} . For the elements with significant excess, the leaching of the elements was calculated according to the penetration equation of Bengtsson 2015. This equation had been proven

valid for several metals that mainly occur as cations. It was assumed to hold for the elements for which a significant excess was observed with the exceptions detailed below. The mean time since deposition was typically 20-40 years, and thus no major average leakage was expected to have occurred. Exceptions detailed below were sulfur, for which significant leakage was judged to have occurred, and antimony for which the extent of leakage was judged to be uncertain; for the non-metal phosphorus no major leakage was judged to have occurred. As mentioned in section 2.2.4, mercury did not meet the assumption that emissions were mainly deposited in the region where they occurred.

- **Sulfur: excluded since total was not measured and leaching is significant.**

According to calculations based on Mylona (1996), the cumulative sulfur emissions in the FOREGS countries 1880-1999 have been 1,01 Pg. The topsoil mass is 1350 Pg, so the cumulative excess concentration without losses would be 750 mg sulfur per kg soil. The measured topsoil excess sulfur concentration is only 170 mg/kg. Two factors may explain the difference:

- a. ***Aqua regia* dissolution only.** The mean subsoil concentration as measured with *aqua regia* dissolution was 262 mg/kg. Total sulfur concentrations may be much larger than the *aqua regia* measured ones; for instance, the earth's crust contains 621 mg/kg. There is thus uncertainty about the ratio of total sulfur concentration in topsoil and subsoil
- b. **Significant leaching from the topsoil.** Several field studies suggest that added sulfur is largely lost through leaching (Andersson *et al.* 2015, Kirchmann *et al.* 2002, Riley *et al.* 2002, Sakadevan *et al.* 1993). The results are consistent with annual losses of the added total sulfur minus 6 kg/ha, with a maximum uncertainty of 15 kg/ha, for additions in the range 6-50 kg/ha. These results pertained to annual precipitation of 700 mm, and agricultural use of soil 20-25 cm deep. The typical additions from emissions to air in the FOREGS countries have been 15-40 kg sulfur per hectare as calculated from the data of Mylona (1996). It should thus be expected that a large share of the deposited sulfur should be leached from the topsoil.

Sulfur was not included in the final analysis.

- **Phosphorus included since leaching loss is small**

Phosphorus is involved in plant metabolism to a very large extent and leaching loss therefore difficult to establish. It is a non-metal, a category that was not represented in the penetration analysis by Bengtsson 2015. Rather small leaching (about 1 kg/ha and year or less) has been reviewed by Bergström *et al.* (2015), confirming similar results by Djodjic *et al.* (2004). In one site of four, the leaching reached 4 kg/ha, year (Andersson *et al.* 2015). No evidence of leaching was found in different long-term field studies (Boitt 2017). The mean soil phosphorus concentration corresponded to

about 2000 kg/ha. Only a quite small fraction of soil P should thus be leached during the emission period and P could be included in the final analysis.

- **Antimony included but to be watched since leaching rate is unclear**

Antimony is a metalloid, a category that was not represented in the penetration analysis by Bengtsson (2015). There are contradictory studies on the long-term behavior of antimony in soils. Ash *et al.* (2013) found less downward mobility for antimony in a shooting range than for nickel. McGregor *et al.* (2015) concluded that Sb was lost from deep soil profiles near an abandoned mine to a larger extent than As, Pb and Fe. Sb was included in the final analysis with the awareness that there might have been significant losses after deposition.

2.3.3 Calculated emissions and topsoil enhancement

The excess topsoil/subsoil concentration ratio, corrected for the ionization energy, was analysed against the potential emissions with the objectives to

- identify elements for which the topsoil/subsoil concentration ratio would have a significant anthropogenic contribution
- enable an initial hypothesis for the dependence of the topsoil/subsoil concentration ratio on the anthropogenically mobilised element mass.

The topsoil excess to subsoil concentration ratio was compared with the hypothetical calculated excess ratio due to emissions from fossil fuel combustion and production and use of the elements. Underlying assumptions were:

- all the mobilised element mass is spread across all soil without containment, and that
- emissions from fossil fuel combustion can be approximated by the emissions from coal combustion.

The calculated excess ratio due to emissions was derived from the following equation:

$$dT/S = (a \cdot P \cdot y + b \cdot C \cdot f) \cdot \tau^{-k} / (M \cdot S) \quad (1)$$

where

dT/S = calculated excess topsoil to subsoil concentration ratio of the element

S = subsoil concentration of the element, mg element per kg soil

a = average emitted fraction from production, use and waste management, in the following called consumption

P = consumed mass of the element in FOREGS countries in the year 1999, Gg

y = number of years resulting when the cumulative consumed mass is divided by the

consumed mass in 1999 (see section 2.2.2)

b = average emitted fraction from coal combustion (final choice 0.8)

C = cumulative used mass of coal in FOREGS countries, (0,508 Pg in 1999 times 100 years to get cumulative mass)

f = fraction of the element in coal, mg element per kg coal

M = mass of topsoil in FOREGS countries (1370 Pg derived from 4.5 Tm² area of the FOREGS countries (Wikipedia), a soil depth of 0.25 m and soil density 1200 kg/m³)

τ = relative element boiling point (boiling point in K divided by 1000) (final choice 1)

k = exponent of power function describing emitted fraction dependence of boiling point (range 0 to 3, see section 2.2.3; final choice 0)

The calculated excess ratio was divided by the measured excess ratio. The spread of this indicator ratio among the elements was studied for various assumptions about emitted fractions and boiling point dependence, and a small spread was searched for. The simplest assumption was selected, neglecting the boiling point dependence ($\tau=1$). A single emitted fraction of 0.8 was chosen for fossil fuel combustion and another, a for consumption of elements. The latter was chosen to minimize the spread of the indicator value while keeping its average value equal to 1.

Once a value of a was selected, the share of the total used mass deriving from combustion and consumption, respectively, were calculated for the selected elements. Elements for which the excess was dominated by emissions from combustion were discussed separately from those dominated by consumption. Equation 2 was applied to give hypothetical excess topsoil to subsoil concentration ratios for the elements for which there were no measured soil concentrations in the FOREGS countries.

2.3.4 Peat concentrations used for proportionality check for topsoil concentrations

A proportionality check for the expected ratio topsoil/subsoil was made using data on earlier surface depositions of elements in Swiss peat (Shotyk and Krachler 2004). These depositions were in the current analysis integrated over a period of 100 years, which would crudely represent the era of industrial use of elements. Data are available for

- scandium, which has had very small increases in deposition over the last 100 years; however, the actual depositions seem to be related to fossil fuel combustion emissions as mentioned under section 3.3.2.
- thallium, which has increased, but for which it has been shown by isotopic analysis that a significant contribution has come from coal burning (Vanek *et al.* 2016), consistent with the fraction 0.999 derivable from Equation 2.

- silver, lead and cadmium which have increased. Consumption data from Europe are consistent with significant contributions to the peat levels.

For thallium and scandium, the measured excess in the FOREGS countries was not significantly different from zero. For silver, lead and cadmium, the calculated excess element concentration in peat cumulated over 100 years corresponds to 0.2 – 0.3 of the measured average excess for these elements for soil in the FOREGS countries. This does not seem unreasonable in view of the location of the peat bog in the middle of Switzerland, far away from the major emissions in the FOREGS countries. It supports the findings that concentrations for some elements have increased measurably in the FOREGS countries due to anthropogenic contributions from human production over the last century.

2.3.5 Hypothetical future soil element enhancement

The global production of elements, mainly retrieved through USGS data (2018) exhibits rather clear trends with a doubling over about 20 years, so it seems likely that this trend will continue over the next 30 years. However, for 9 elements, air emissions in Europe have been reported (EMEP 2018). In the period 1990-2015, the emission reductions have more than offset the increased use of elements. Additional depositions beyond 1999 were predicted, assuming the average fractional emission reduction would continue. All estimates are uncertain, not the least since some sources may not have been accounted for.

2.3.6 Enhanced element concentrations in soil in relation to sewage sludge

Soil amendment with sewage sludge is a common practice in many countries. For instance, in several countries, more than one-half of produced sludge has been used to amend agricultural land (European Commission 2015). Much effort has been devoted to decreasing enhanced element concentrations in sludge. In Europe, a sewage sludge directive from 1986 (86/278/EEC) sets limits for sludge and soil for several elements (cadmium, chromium, copper, lead, nickel, and mercury). More far-reaching restrictions have been proposed in Sweden and are echoed in the long-term intentions of the Swedish quality system for sludge, REVAQ (Svenskt Vatten, 2018). The restrictions purport to cause no more than doubling of natural soil metal levels in 500 years (as proposed by Naturvårdsverket 2013), although for zinc, copper, cadmium and nickel, regulatory levels have replaced the intended levels. To illustrate the present state of play, comparisons were made of concentrations of elements in sewage sludge

- as measured in Sweden 2016
- due to the unavoidable sludge components from human dietary intakes, and
- as stipulated in the quality system.

The metric used is the enhancement of element levels if the sludge were applied to average European soils (FOREGS 2005) at an annual rate of 1 Mg/hectare integrated over 500 years with no leaching loss.

2.4 Enhanced levels in sewage sludge

The analysis serves above all to illustrate the anthropogenic component of elements in sewage sludge. The analysis sets out from the unavoidable sludge concentrations due to human dietary intakes of elements, dealt with in section 2.1. In a similar way as for the topsoil analysis, contributions from coal combustion and element consumption were accounted for. The total sludge level of an element would be

$$T=H+a*P+b*C \quad (2)$$

T = total sludge concentration of an element, mg of element per kg of sludge dry matter

H = mean contribution to the sludge concentration of the element from unavoidable natural human intake as found in section 3.1, mg of element per kg of sludge dry matter. The daily dietary intakes were converted to sludge levels via the assumed 70 g of dry sludge per person per day.

P = country consumption of the element, thousand Mg per year (see section 2.2.1)

a = fraction of the consumed element that reaches sewage sludge per unit sludge mass, mg of element per kg of sludge dry matter per thousand Mg of the element produced per year. This fraction is assumed to be approximately constant across elements

C = country consumption of coal, thousand Mg per year.

b = fraction of the element mobilised in coal that reaches sewage sludge per unit sludge mass, mg of element per kg of sludge dry matter per thousand Mg of the element combusted in coal per year. This fraction is assumed to be approximately constant across elements. The amount mobilised is the average fraction of the element in coal, (see section 2.2.1) times the mass of coal consumed in the country

2.4.1 Data sources for sludge concentrations

Two extensive sets of sludge concentration T were used for investigating the outcome of Equation 2. The first set comprised data on mean sludge contents of 70 elements from 48 Swedish sewage treatment plants (Eriksson 2001), collected in the year 2000.

The second set pertains to sludge ash contents of 54 elements (Krüger and Adam 2014). Their ash samples were obtained in 2011 from 22 sludge incinerators representing 97 % of German sludge ash. In this case two assumptions are needed to translate ash levels of elements to dry sludge levels:

- Some elements will be lost in the incineration and ash sampling. Krüger and Adam (2014) show mass balances for three incinerators for 7 elements. The retrieved mass fraction varies between 0.36 (Hg) and above 1 (Cr, Ni, Cu, Cd, Pb) with a median fraction of 0.8. The authors emphasize that the mass fractions are quite uncertain. For the current assessment, a mass fraction to ashes of 0.8 is assumed.

- The mass of ashes needs to be translated to dry mass of sludge. A few pieces of information from Krüger and Adam (2014) suggest an ash weight of 20-50 % of that of dewatered or dried sludge. Eriksson (2001) provides detailed data on loss on ignition for all sludges, with a mean loss of 62 %. The implied ash weight of 38 % of the dry sludge weight is consistent with the few data given by Krüger and Adam (2014). For lack of better data, it is used to estimate the dry sludge mass.

The concentration in sludge is then assumed to be 0.38/0.8 or 0.475 of that of ashes.

A third piece of information relates to time series of element concentrations in Swedish sewage sludge (Kirchmann *et al.* 2017). The series covers fully or partly the time period from 1960 to 2010 for sewage works in 4 major cities (Uppsala, Gothenburg, Stockholm and Malmö/Lund) and from 1985 also a Swedish average. Concentrations of Ag, Cd, Cu, Hg, Pb, and Zn were approximately constant 1960-1975 and thereafter declined strongly to reach a relatively constant level after the year 2000. The cumulative concentration was approximately 100-500 times the concentration in the year 2012.

An additional set of element concentrations in Swedish sludge in 2016 was made available from Svenskt Vatten (Anders Finnson personal communication 2017). The information came from 41 not identified sewage treatment installations participating in the certification program. It covered more than one-half of the municipal sludge volume in 2016 but was not representative in the way that the data from Eriksson (2001) were. Still, the average should give a very good indication of the mean Swedish concentrations.

2.4.2 Deselection of elements from the analysis

Several elements are exempt from restrictions for soil amendment with sewage sludge according to the Swedish quality system REVAQ (Svenskt Vatten 2018). These include the macroelements mentioned under 2.1.1. Those were present in Swedish sludge in the year 2000 in concentrations above 0.3 % (Eriksson 2001), excepting concentrations of Cl and N that were not reported. The macroelements are not included in the current analysis for the German nor for the Swedish study. Explicitly exempted in Sweden are also Au, B, Bi, Br, Co, I, Mn, Mo, Os, Se (enumerated in the tool for sewage plants but not assigned limits for amendment). These should have been present in Swedish sludge in the year 2000 in average concentrations below 0.03 % (Eriksson 2001); Os and I were not measured. There may be different reasons for not giving them priority in REVAQ, but they are judged to be of interest in the current analysis. The latter also holds for rubidium. Finally, for indium the sludge concentration is less than twice the dietary contribution, which is barely a significant excess, and indium is thus also excluded. Rubidium and indium were not measured in the German study.

2.4.3 Influence of consumption and fossil fuels

The ratio $R = (T-H)/(a*P+b*C)$ should be equal to 1 if T has no other components than those of Equation 2. In reality, there should be many more components. Their significance can be

elucidated from the variations in the ratio if a and b are found by iteration, keeping $R=1$ and minimizing its variation among elements. The iteration will give differing results if arithmetic or geometric mean and ditto relative standard deviation among elements are used. The geometric ones are chosen since the ranges are very large; arithmetic means would strongly favour large concentrations and arithmetic standard deviations would strongly favour very large deviations. For both the Swedish and the German data, use of arithmetic means and variations would result in optimal curves where the largest predicted concentrations would grossly overestimate the measured ones.

2.4.4 A non-negligible share of emitted mass should be collected in sewage sludge

There are several reasons why a significant share of emissions to air should be found in sewage sludge: emissions are locally deposited and washed out with storm water (rain water), a considerable share of storm water often goes to sewage treatment, and the storm water has similar element concentrations as the wastewater. Some reasons are detailed below.

- Emissions to air tend to be deposited at distances of the order of less than 100 km from the emission point, as mentioned in section 2.2.4. Depositions should thus be expected to occur near large population regions.
- Historically, sewage systems have used combined channeling for wastewater and stormwater. Only in the last decades has there been a tendency to separate channeling.
- In the city of Stockholm, about one-half of the sewage channeling system for stormwater is combined with the ordinary sewage system that leads to the sewage plants; the other half goes separately to recipients (Stockholm city 2015). A relatively large share of the ground deposition would thus be expected to be collected to the sewage plants.
- The collected stormwater would on average have about the same concentration of elements as the incoming water to a sewage plant. As an example, 10 trace elements in stormwater, collected at a population center outside of Stockholm, on geometric average had the same concentration as the incoming water to its sewage plant (calculated from Alm *et al.* 2010 and Pettersson and Wahlberg 2010).

2.4.5 Hypothetical concentrations in sludge in Sweden and Germany

Extensive data are available on contents in sludge in Sweden (Eriksson 2001) and Germany (Krüger and Adam 2014). As a calculational exercise, hypothetical concentrations due to consumption of elements and combustion of fossil fuels in the two countries were derived. In addition to the assumptions in table 1 below, the following assumptions were made.

- The mean sludge generation is 26 kg per person per year across the globe.
- Emissions to sludge were proportional to the consumption of elements in the

countries

- Consumption of elements was assumed to be the global production in the year of sludge measurement scaled by the national gross product divided by the global gross product in constant US dollar (World Bank 2017)
- 1 Mg of coal oil equivalent corresponds to 1.42 Mg of hard coal
- Of all petroleum products, 15 % are heavy fuel oil. One Mg of such oil corresponds to 0.5 Mg of coal with respect to emissions to sludge.

For the estimation of sludge trends for the future see above section 2.3.5

Table 1. Numerical assumptions used for calculations according to Equation 2. Sources for the data: Coal and oil: BP 2018; GDP: World Bank 2017; Population: World Bank 2018.

	Population, million inhabitants	GDP constant 2010 million USD	Coal consumption, thousand Mg	Oil consumption. thousand Mg
Sweden 2000	8,9	396 000	2 960	11 000
World 2000	6 130	49 900 000	3 400 000	
Germany 2011	80	3 540 000	260 000	110 000
World 2011	7 010	68 000 000	5 500 000	

2.5 Effects of enhanced concentrations of element in soil

A review of the effects of enhanced soil concentrations of elements is beyond the scope of the current review. It is however interesting to know if there is any effect at all. In the following some examples are given about no effect concentrations in soil.

For effects on soils for 11 elements, the Ministry of the Environment, Finland (2007) has provided threshold values that were given a prominent place in the recent assessment of European soil contamination (Toth *et al.* 2016). Another set of thresholds for 7 of those 11 elements was proposed in a joint European effort (JRC 2006). The latter set was elaborated with different thresholds for the pH ranges 5-6, 6-7 and >7, and comparison was made with an EU directive pertaining to pH 6-7 which is a common range of pH for agriculture. The proposed threshold for pH>7 was typically twice the threshold for pH 5-6, so the pH dependence was moderately large.

For the 7 common elements, the JRC thresholds for pH 6-7 are in the range 0.5-1.17 of the Finnish ones. Somewhat higher thresholds were found in long term multi-soil experiments in the United Kingdom (UK Water Industry Research Limited 2007) where no effect on soil microorganisms was found after exposures corresponding to 1.4 times of the Finnish

thresholds (Cu and Zn) and 3 times (Cd), respectively.

To enable extrapolation to elements beyond those listed, the Finnish thresholds were fitted to a relation with the mean European soil concentration and the geometric mean of the first three ionization energies of the 11 elements (unit eV). The latter quantity had proven to be relevant in the quantifications of the topsoil to subsoil concentrations (section 2.3.1) and the diet/soil ratio (section 3.1.1 Table 2). The Finnish thresholds were fitted to the product of a power function of the soil concentration and a power function of the ionization energy. The smallest relative standard deviation of the ratio stated/calculated threshold was obtained for a soil concentration power of -0.07 and an ionization energy power of 4.72. For elements not included among the Finnish set, these power functions were used to calculate assumed thresholds.

3. Results and discussion

The results encompass

- measured dietary intakes of elements and their relation to soil concentrations of elements
- measured excess element concentrations in European topsoil as compared to subsoil and their links to fossil fuel combustion and consumption of elements, and a brief discussion about stream sediments
- measured element concentrations in Swedish and German sewage sludge, their links to fossil fuel combustion and consumption of elements, and the concentrations entailing sludge amendments of European topsoil
- extrapolations of topsoil and sludge concentrations to elements for which no measurements are available and to future years until 2045
- environmental effects of enhanced element concentrations in topsoil.

3.1 Dietary intakes

The detailed data on dietary intakes including literature references are given in the Appendix. In the current section, the dietary intake of an element is related to the level of the same element in the topsoil, hereafter referred to as the diet/soil ratio. Figure 2 gives this ratio and the geometrical mean of the first three ionisation energies. This parameter was introduced on the assumption that an element with low ionisation energies would tend to react rapidly with other elements in soil, leaving less room for the same element to be partitioned to pore water; higher ionisation energy might lead to more partitioning to pore water and subsequent uptake by plants eaten by man.

3.1.1 Dietary intakes depend on many element properties

Figure 2 shows that a change in ionisation energy frequently correlates with a much larger

relative change

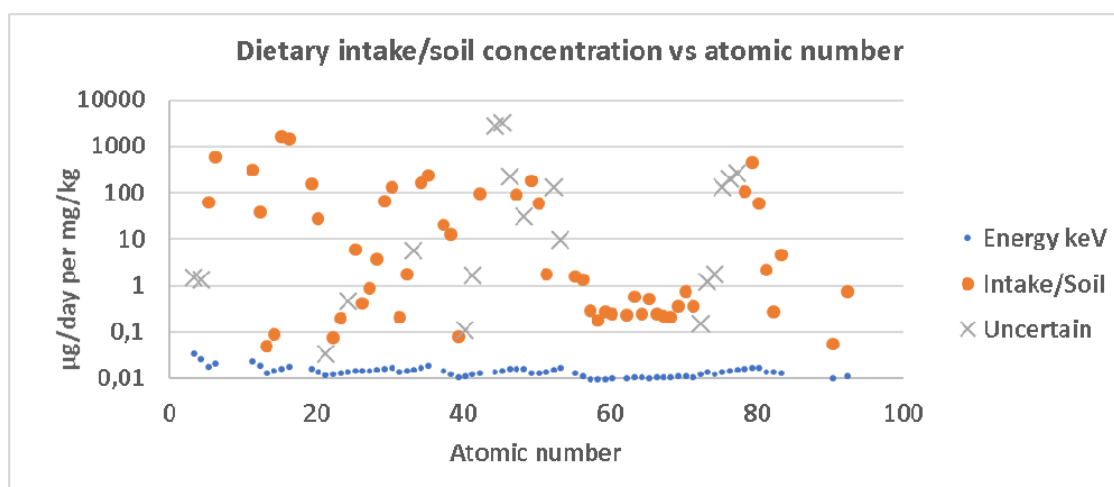


Figure 2. Dietary intakes of elements divided by soil concentrations versus atomic number.

The ordinate gives the ratios of the mean daily dietary intake ($\mu\text{g}/\text{day}$) and the topsoil concentration (mg of element per kg topsoil). In most cases the ratios would be accurate within a factor of 3 (orange points). In some cases, however, data sets for one element are more variable or at most one source of dietary intake could be found (crosses). The ionisation energies (lowermost points) are the geometrical mean of the first three ionisation energies (keV).

In the same direction in the diet/soil ratio (e.g. increases for elements 21-25, 26-30, 39-44, 72-76, and the 100-1000 times decrease in the diet/soil ratio for elements 20 \rightarrow 21, 30 \rightarrow 31, and 38 \rightarrow 39). Many properties of the elements, however, may influence the diet/soil ratio. Sometimes the different properties are correlated with one another, such as ionisation energy increasing with atomic number, density increasing with boiling point, or low boiling point associated with high ionisation potential. Some of the more important properties are the following:

- The diet/soil ratio is often strongly related to the ionisation energy. In the simpler cases of alkali metals (only one dominant ionisation energy) and alkaline earth metals (two energies) the dependence is very clear, apart from the special cases of the second and third period of the periodic system.
- The properties of soils are strongly influenced by Al, Mn, and Fe, not the least because their oxides are typically nanosized (Barron and Torrent 2013).
- Iron has influenced the highly siderophile (“iron-loving”, Goldschmidt 1937) elements Ru, Rh Pd, Re, Os, Ir, Pt and Au in the formation of the earth. Those have very low abundances in soil and very high diet/soil ratios.
- The electron affinity may be related to the ratio diet/soil. The electron affinity is

negative for the elements preceding group 13 elements: Be, Mg, Zn, Cd, and Hg, as well as for Mn. Often but not always high electron affinity is concomitant with high diet/soil ratio and low affinity with low diet/soil ratio.

- The maximum oxidation number varies systematically across the periodic system, often in a similar way as the first ionisation energy.

Some relations between the diet/soil ratio and various parameters are given in table 2. For elements in groups 9-17 of periods 5 and 6 there is a large scatter in their dependence on atomic number or ionization energy.

Since the observations in table 2 were not within the primary scope of the current review, it should be a matter of further research to find chemical parameters that can help define more precise relations between the diet/soil ratio and such parameters. Figure 3 shows one very interesting feature for further exploration: a large drop in diet/soil ratio pertaining to elements 25-27 (Mn, Fe, Co). There is a drop in dietary intake of about a factor of 1000 between elements 26 and 27, which is matched by a similar drop in topsoil concentration. The drop in the diet/soil ratio occurs between elements 25 and 26 and is about a factor of 30. Similar discontinuities can be observed for elements in mothers' milk (Björklund *et al.* 2012) and soil-plant transfer factors (Jolly *et al.* 2013, IAEA 2010, Uchida *et al.* 2007).

Table 2. Correlations between the diet/soil ratio D and various parameters for groups and periods of the periodic system of elements. The constant k can be different for the different relations. R^2 is the coefficient of determination. The designation *Uncertain D* refers to elements for which D is judged to be uncertain to more than a factor of 3; this pertains also to As, Pd, Cd, Te, I, Ir, and Pt for which there is no table row.

Group	Period	Parameter	Relation	R^2	Uncertain D
	2 and 3		None found		Li Be
1 Alkali metals	4-6	First ionisation energy i_1 eV	$D=k*i_1^{41.4}$	0,99	
2 Alkaline earth metals	4-7	Geometrical mean of the first two ionisation energies i_{12} eV	$D=k*i_{12}^{18.9}$	0,96	
16	3-5	Geometrical mean of the first three ionisation energies i_{123} eV	$D=k*i_{123}^{19.4}$	0.97	
13-16	4	Atomic number A	$D=k*A^{64.1}$	0,94	
13-16	4	Geometrical mean of the first three ionisation energies i_{123} eV	$D=k*i_{123}^{34.4}$	0.98	
3-7	4	Atomic number A	$D=k*A^{31.2}$	0,95	Sc, Cr

3-7	4	Geometrical mean of the first three ionisation energies i_{123} eV	$D=k*i_{123}^{25.6}$	0,93	Sc, Cr
8-12	4	Atomic number A	$D=k*A^{44.9}$	0,96	
8-12	4	Geometrical mean of the first three ionisation energies i_{123} eV	$D=k*i_{123}^{36.2}$	0,96	
3-8	5	Atomic number A	$D=k*A^{103}$	0,98	Zr, Nb, Ru
3-8	5	Geometrical mean of the first three ionisation energies i_{123} eV	$D=k*i_{123}^{41.5}$	0,90	Zr, Nb, Ru
4-8	6	Atomic number A	$D=k*A^{142}$	0,92	Hf, Ta, W, Re Os

3.1.2 Dietary intakes reflect the odd-even variation of the lanthanides

Another interesting feature is related to the odd-even variation of the lanthanides. Due to nuclear properties influencing the creation of the universe, lanthanides with even atomic numbers are more abundant in the earth's crust than lanthanides with odd atomic numbers (Cotton 2006). Elements with even atomic number typically have 4 times higher concentration than neighbours with odd number. This is also closely reflected in the topsoil element concentrations. The dietary intakes are somewhat less influenced by the odd-even relation. The diet/soil ratio is not significantly different between elements with odd and even atomic number. The phenomenon is not apparent in the ionisation potentials which relate to the atomic electron shells, while the odd-even variation is due to an atomic nuclear property.

3.1.3 Dietary intakes have parallels in plant bioaccumulation and in partitioning coefficients

The strong correlation between dietary intakes of an element and element chemistry parameters (figures 2 and 3, table 2) has a counterpart in plant uptake and pore water partitioning. This is brought out in figure 3 and in the discussions below.

Human dietary intake relates to a large extent to plant intake. Bioaccumulation between soil and plants is very variable, dependent on for instance plant species and soil conditions; Smith and Huyck (1999) have enumerated 39 relevant parameters. Generalised bioaccumulation factors for plants have been compiled by Smith and Huyck (1999) who named them indices of bioaccumulation, defined as the ratio of the element concentration in plants to the concentration in soils (dimensionless, for instance the ratio of element mass per unit plant mass and element mass per unit soil mass). They were based on early work that was later followed up by Kabata-Pendias and Mukherjee (2007) who discussed index of bioaccumulation. The generalized indices of bioaccumulation have been entered in figure 3 for elements with atomic numbers 21-30. The pattern is very similar to that of the diet/soil

ratio although the spread of the data is larger. Such similarities are found across the periodic system.

Plants absorb elements available in pore water. The partitioning coefficient K_d gives the fraction going to soil particles relative to pore water. Its inverse should thus describe the ability of plants to get access to elements. Data are available for about 200 soils in Ontario used for agriculture (Sheppard *et al.* 2007). The trends of this inverse versus atomic number are similar to the trends of the diet/soil ratio for all except a handful of the 40 elements for which both partitioning coefficients and diet/soil ratios were available (similar for elements with atomic numbers 11-13, 25-35, 48-55, the lanthanides 57-71, 80-81 and 90-92). Partitioning coefficients have extremely large ranges of many decades, so the spread of the ratio diet/soil to inverse is rather small.

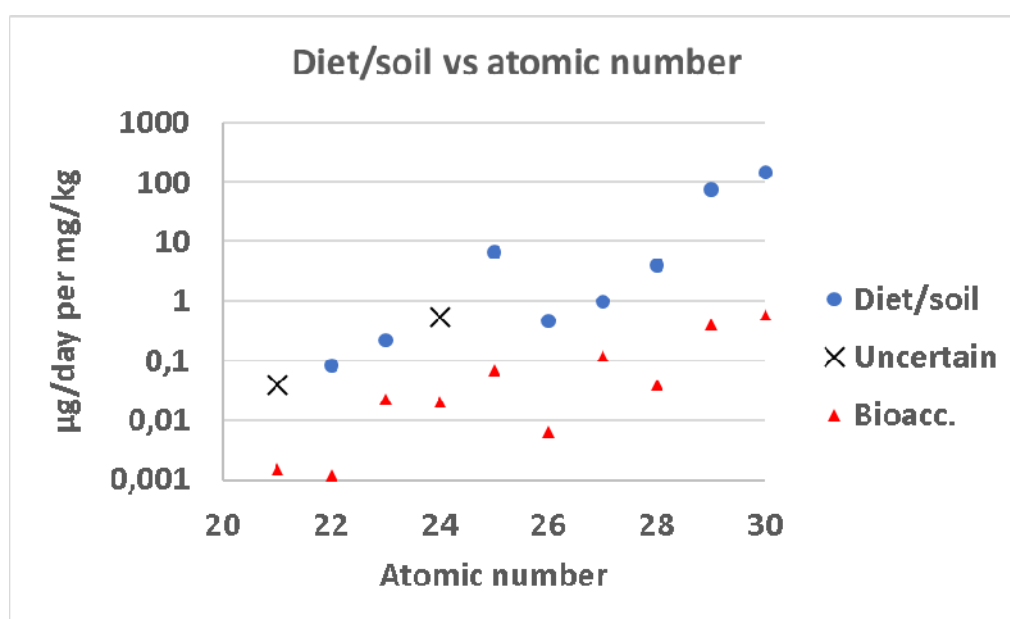


Figure 3. Atomic number dependence of the ratio of dietary intake and topsoil concentration for elements 21-30. The crosses mark elements for which the information about dietary intakes is uncertain. In particular, for element 21 (scandium) a contamination of the soil is very likely, which might have entailed a several times lower diet/soil ratio than in the figure. Also shown are the dimensionless generalized indices of bioaccumulation of Smith and Huyck (1999) discussed in section 3.1.3.

3.2 European topsoil levels of some elements reflect global combustion and consumption

The excess topsoil element concentration was predicted based on the emission from production, use and waste management of elements, in combination with emission of elements in consumed coal (section 2.3.3). The prediction was used to assess the current enhancement of soil contamination as well as predict enhancements for elements not yet measured and extrapolate to future soil concentrations. A brief comment is also made on enhanced element concentrations in stream sediments.

3.2.1 Factors behind measured enhancements

The measured mean excess topsoil/subsoil concentration ratio is given in figure 4 as a function of the predicted ratio, for those elements for which there was a prediction of significant excess diet/soil ratio (above 0.05). The mobilised element mass should be seen as a very approximate proxy for the economic activity in society disregarding other important factors. It is for instance quite likely that large contributions to the enhancements come from use of artificial fertilizers in agriculture for Cd, and from a legacy from use of leaded gasoline for Pb.

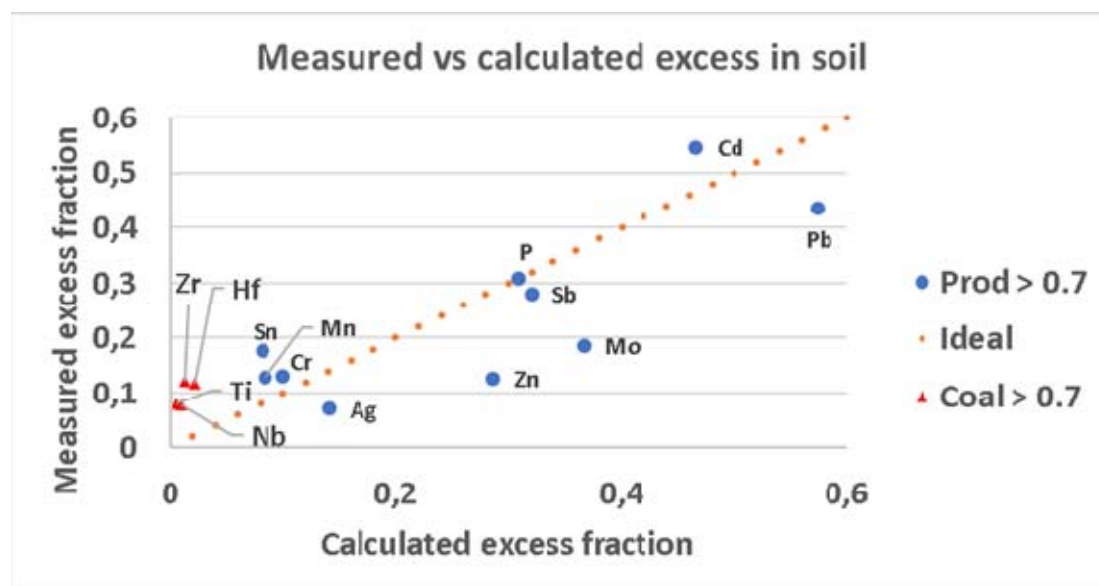


Figure 4 (above). Measured versus calculated excess fractions of elements in European topsoil. In the calculations it was assumed that one emitted fraction applied to combustion of fossil fuels, and another to element consumption (see section 2.3.3 for details). The dotted line represents equal measured and calculated fractions. For elements represented by triangles, more than 70 % of the calculated emitted mass to air was derived from combustion of fossil fuels. For elements represented by circles, more than 70 % of the calculated emitted mass to air was derived from production, consumption and waste management of elements. For reasons given in the text, S and Hg which had significant excesses were not entered in the diagram.

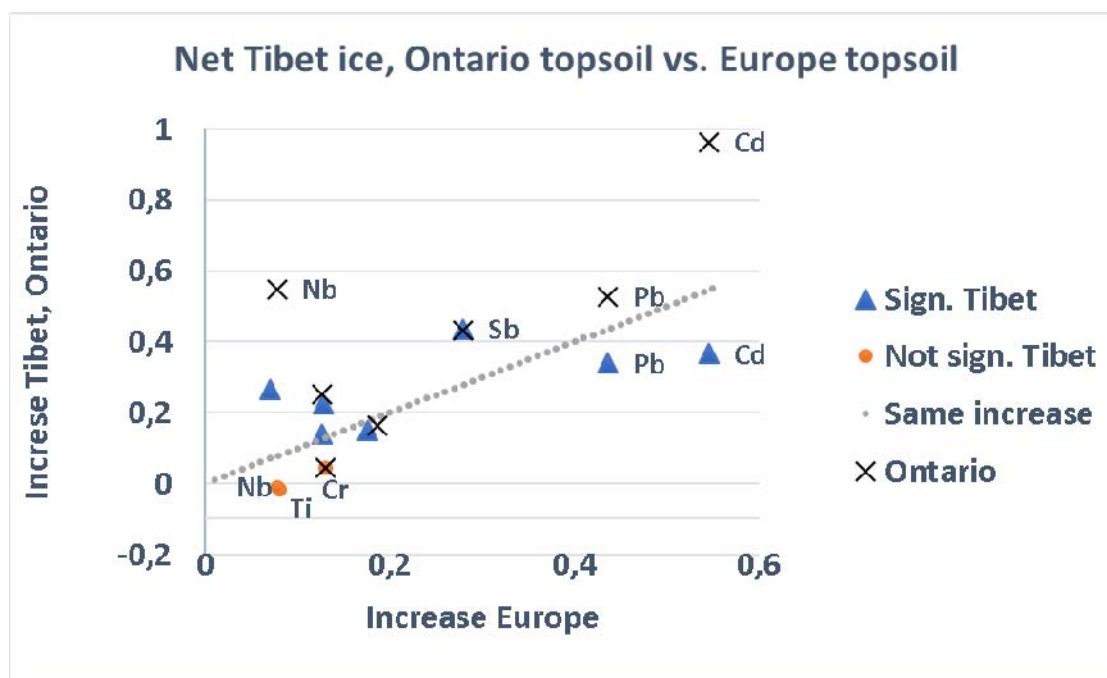


Figure 5. Comparison of increased element concentrations over a century for Tibet ice (Beaudon *et al.* 2017), Ontario topsoil (Sheppard *et al.* 2009) and European soil (FOREGS 2005). The dotted hypothetical line indicates the same increase in Tibet, Ontario and Europe. For the three lowest points (Ti, Nb, Cr), the increase in Tibet was not statistically significant. There are several differences between the three data sets, as discussed in the text.

Sulfur and mercury omitted, antimony not aberrant. Sulfur is omitted from figure 4 since sulfur contents in coal are very variable and highly regulated, total sulfur in soil was not measured and sulfur leaches to a large extent from topsoil (compare section 2.3.2); the measured excess fraction in topsoil was 0.67. Mercury is omitted since it is transported over very large distances and deposition does not to a good approximation occur near the point of emission (section 2.2.4); the measured excess fraction in topsoil was 0.75. Questions were raised about the possible leaching of antimony from topsoil (section 2.3.2) but figure 4 gives no suggestion of an aberrant excess concentration of antimony in topsoil.

Enhancements similar in Switzerland, Tibet and Ontario. The increase demonstrated in figure 4 is congruent with the data calculated from the Swiss peat bog (section 2.3.4). It is also similar to data from Tibet ice (Beaudon *et al.* 2017) and Ontario topsoil as shown in figure 5.

The Ontario (Sheppard *et al.* 2009) data refer to the ratio of concentrations in 0-15 cm topsoil over 30-60 cm subsoil, corrected for ionisation energy in a similar way as the FOREGS data. The 59 soils were agricultural and *aqua regia* digestion was used, which might make comparison with the FOREGS data less relevant; the latter were all based on total extraction. The alkaline earths were to a large extent lost from the topsoil; a similar trend prevailed for the FOREGS soils. Also Th was lost. It should be a matter of further research to elucidate why nearly the same elements appear in all locations and with similar degrees of

enhancement. One intriguing feature is the concomitant large variation in Nb excess and the extreme steepness of the atomic number dependence (elements 39 Y to 44 Ru with power 103 in Table 2).

Long-term loss from topsoil possible. The baseline enhancement ratio behind figure 4 is not 1 but 0.96. Even if topsoil and subsoil had the same elemental composition at their creation, a loss from the topsoil would be expected. Initially in unamended and tilled soil it would correspond to about 1 % per year (Bengtsson 2015), and it might subside in coming decades. A 5 % loss over time for a collection of very varied soils would be in line with a loss from topsoil that approaches equilibrium over a number of decades. Similarly, the baseline ratio for the Ontario data is 0.87 which is reasonable since the Ontario topsoil depth is 15 cm, likely to experience a larger loss than the 25 cm depth of the FOREGS soils.

Reported emissions insufficient to explain soil enhancements. The mean topsoil concentration was clearly enhanced (>10 %) for 11 elements: Cd, Pb, P, Sb, Mo, Sn, Cr, Mn, Zr, Zn, and Hf. This can be compared with air emission estimates. Emissions in Europe have been estimated for zinc, lead, and cadmium for the years 1990-2015 (EEA 2017a). These were extrapolated to 1900-2015 (section 2.3.5). If all emissions had gone to European soil at the time of the FOREGS measurements, the soil level enhancement would have been 7 %, 13 %, and 7 %, respectively for zinc, lead and cadmium. The emissions are thus not sufficient to explain the enhanced soil levels. It has previously been observed for cadmium and lead that official reported emissions estimates in modelling in the EMEP region have resulted in significant (2-3 times) underestimation compared to measurements (EMEP 2007). For air concentrations, deficits have been found for lead and cadmium (7 % and 21 % accounted for, respectively) in addition to deficits for arsenic, chromium, copper, zinc and nickel (Dore *et al.* 2014). In that case, the underestimation was attributed to wind-driven re-suspension of surface dust.

Many sources besides air emissions. Other sources than air emissions have been discussed above all for agricultural soils. In 2016, air emissions contributed a smaller part to the cadmium balance of agricultural soils (European parliament 2017). For farms in Germany and the Netherlands around the year 2000, atmospheric deposition accounted for most of the lead input, for intermediate fractions (about 20 %) of chromium, nickel and zinc inputs, and for small fractions (a few per cent) of inputs of copper, for which organic fertilizers were completely dominating (AROMIS 2018). In the sampling of FOREGS soils, however, it was recommended that soils disturbed by agricultural activities be avoided, so other sources than air emissions might not be so important. Still, the non-agricultural soils might have contributions from other sources than air emissions due to wind-driven re-suspension of surface dust.

Ilyin *et al.* (2004) have estimated emissions and deposition for Europe for the years 1980-2000. They found an average deficit of only 25 % for lead, and insignificant for cadmium, with larger deficits in earlier years.

3.2.2 Extrapolation suggests significantly enhanced concentrations in topsoil for 9 further elements

Application of the same analysis as above to elements not studied in the FOREGS survey suggested that mean excess concentrations of 10-50 % might have been expected in 1999 for Ge and Ir and beyond 50 % for 6 other elements (Rh, Re, Pd, Au, Pt, Ru) of which Re would have a calculated excess of 3.0 and Rh of 4.2 times the mean concentrations.

For all elements except gold, the dominant emission would have come from fossil fuel combustion. The 8 new elements have high boiling points in the range from 3081 K for gold to 5900 K for rhenium. In recent years the emitted fractions may have been much lower than the assumed 0.8 for combustion and 0.06 for consumption. The calculated excesses might thus be overestimated. They are however supported by the finding by Sen and Peucker-Ehrenbrink (2012) that global anthropogenic fluxes for all 8 elements except Ge exceed natural fluxes; the other non-gaseous elements mentioned by Sen and Peucker-Ehrenbrink (2012) are chromium and antimony which appear in figure 4. A high emission is also supported by measurements in a small coastal village on Cape Cod, Massachusetts, U.S.A., where 69 % of the total airborne osmium is of anthropogenic origin (Sen *et al.* 2013). Further, residential coal combustion has been shown to give large contributions to emissions of Pd and Pt in the atmosphere of Changji city, China, (Liu *et al.* 2015), and platinum group element emissions at urban and remote locations reflect contributions from several sources (Rauch and Peucker-Ehrenbrink 2015).

3.2.3 Trends for future soil concentrations

Additional depositions for the period 2000-2045 were estimated, based on measured emissions 1990-2015 (EMEP 2018) for 5 elements (Cd, Hg, Pb, Se, Zn). The additions were judged to become smaller than the depositions already accumulated. This is also expected to hold for the 7 other measured elements (Cr, Hf, Mo, Mn, P, Sb, Sn, Zr). In addition to the 12 measured plus 8 not measured (calculated) elements surpassing 10 % excess in 1999, 2 new elements (Ag and Cu) might be added to the list in the period 2000-2045. In that period, the concentrations of gold and possibly also ruthenium and palladium might attain several-fold enhancement which may be of concern (section 3.4).

3.2.4 European stream sediment levels of some elements reflect global combustion and consumption

The corresponding analysis for stream sediment revealed a much larger spread among elements and a much stronger dependence on ionisation energy, with smaller stream excesses for higher ionization energies. Most of the element having significant excess ratios in soil also exhibited significant excess ratios in stream sediments. Copper had an aberrant pattern, exhibiting significant excess ratio in stream sediment but not in topsoil. As expected, the highest excess fractions in stream sediments (Cd and Zn) were higher than those in topsoil: 2 and 1.4 versus 0.5 and 0.13, respectively. The average stream excess ratio was about 7 times higher than the topsoil excess ratio. Since the spread was quite large, no further

analysis was performed

3.3 Sludge levels of elements are enhanced beyond the unavoidable contributions from human excreta

First in this section, the dietary component of sewage sludge is compared with measured levels which include non-dietary components. Thereafter, possible quantifications are sought for any significant non-dietary components.

3.3.1 Element levels enhanced up to 600 times

The sludge element concentrations are more than a hundred-fold enhanced in comparison with the dietary component for 20 elements in the Swedish study 2000 and 19 elements in the German study (figure 6), in addition to the deselected Al and Fe. The reasons for the enhancements were sought.

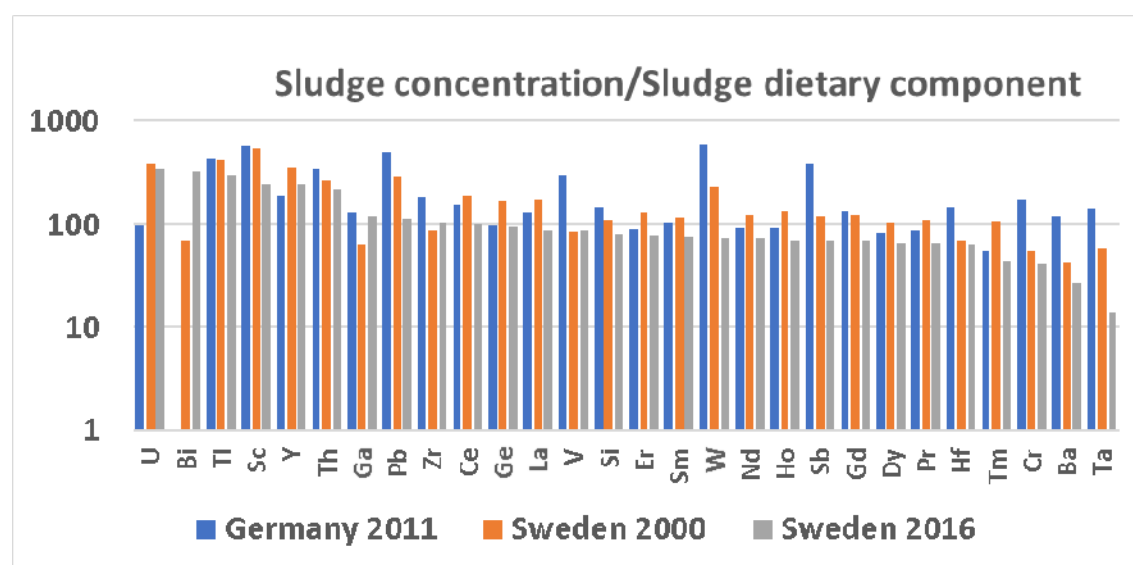


Figure 6. Ratio of mean national sludge concentration of some elements and the unavoidable dietary component of the sludge due to human intakes. The elements are ordered according to the extent of the enhancement in Sweden 2016. Only the elements with at least one enhancement above 100 are entered in the diagram. Some deselected elements (section 2.4.2) also had high enhancements, e.g. Al and Fe in the range 300-900. Sludge data are based on Eriksson 2001, Krüger and Adam 2014, and Finsson (Personal communication 2017).

Enhancements over the dietary minimum approach a factor of 600. A similar large enhancement can be derived from Swiss peat data (Shotyk and Krachler 2004) for scandium. In all three cases of figure 6, titanium is enhanced more than 300 times, consistent with its abundant use in products likely to be highly channeled to sludge. For most of the elements with very high enhancement factors, the dietary intake is comparatively small, and any risk is also small.

The median German element concentrations in sludge in 2011 were 1.8 times higher than the

Swedish ones in 2016. The largest differences pertained to Ta (German level 10 times the Swedish one) and U (0.28 times). Sweden has for decades worked on reduced contaminant levels in sludge, and comparatively low levels might be expected. The median enhancement of the Swedish data in 2016 was 0.65 of that from the year 2000, and the only clear increase was for Bi (about 5-fold). In 2016, only 9 elements had more than 100 times enhancement, as compared to 20 in the year 2000

3.3.2 Amounts emitted to air are similar to amounts in sludge

In order to find the reasons for enhancements given in figure 6, the contributions to the sludge concentration from combustion and consumption were calculated according to Equation 2 for German sludge. The unavoidable contributions from human excreta as described in sections 3.1.1 and 3.1.2 were subtracted from the measured concentrations. The net concentrations are plotted in figure 7 against the calculated ones for the parameters that gave the minimum variation among the 39 non-macro-elements of Krüger and Adam (2014). The parameters found were $a=0.0026$ for consumption and $b=0.0063$ for combustion. The geometric standard deviation of the ratio measured/calculated was 2.12. The 12 elements with the lowest global production volumes (Sc, Ho, Lu, Tm, Yb, Tb, Ge, Eu, Th, Ga, Er, Dy) all had an estimated coal contribution share of the sludge concentration above 0.91 of the mobilized mass. For the platinum group elements Rh, Pd and Pt, measurements were made only for about 80 % of the ashes entailing poorer representability than for the other elements.

Sludge concentrations depended little on the boiling point. According to figure 1, the boiling point influences the element air emissions to power -2.8. No such dependence could be found for sludge, so figure 7 is calculated on the basis of no boiling point dependence.

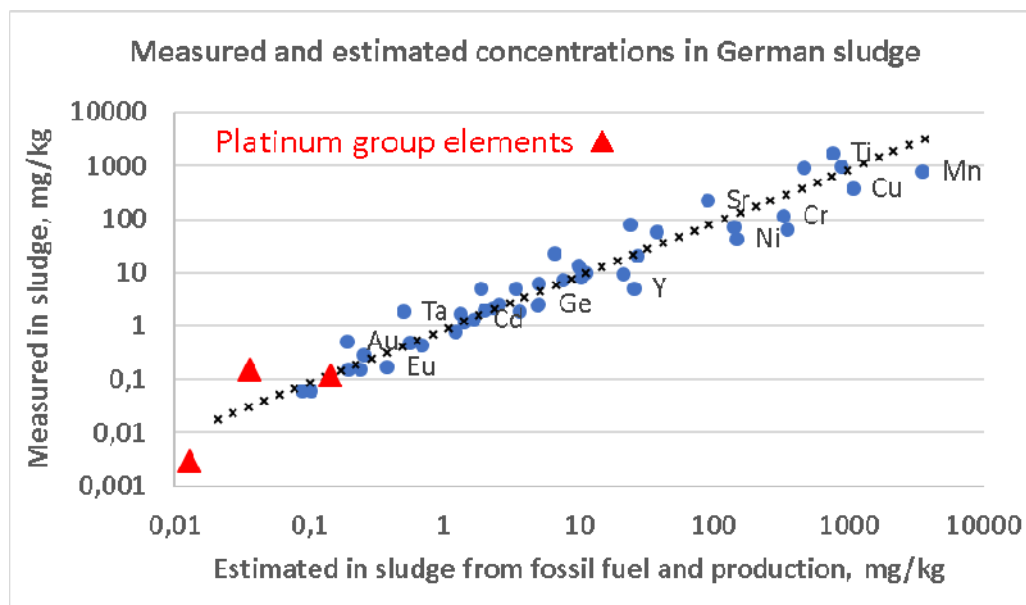


Figure 7. Net concentration of elements as a function of the assumed contributions from global consumption and fossil fuel combustion. Each of the 62 circles represents one element. The dotted line represents the case that the

assumed contributions equal the measured ones. For 3 platinum group elements there were fewer measurements than for the other elements.

A calculation similar to that behind figure 7 was performed for Swedish conditions in the year 2000. A similar picture emerged but with much larger spread of the points. This would be consistent with the much smaller economy of Sweden compared to Germany, entailing much larger deviations from the hypothesis of production being proportional to the gross domestic product for all elements.

The calculated hypothetical emitted fractions can be compared with the few available estimates of emitted fractions detailed in section 2.2.5. These are in the range about 0.0002-0.01, as extrapolated to the year 2011. This range is not consistent with the hypothetical range 0.0026-0.0063, considering the scarcity of emission data and the large uncertainties. The estimate for the European emissions from 2014 of 0.0002-0.014 (except mercury) may be underestimated by about a factor of 3 (section 2.2.3), which would suggest a true emitted fraction about 0.0006-0.04, encompassing the full hypothetical range 0.0026-0.0063. The contention of a non-negligible share of air emissions going to sludge, supported in section 2.4.4, is also supported by the design of sludge generation technology (section 2.2.3). At the same time, the absence of a boiling point dependence in the calculated sludge concentrations suggests that many sources besides air emissions contribute to the mass of natural elements in sludge.

3.3.3 Impact on agricultural soil of enhanced element levels in sewage sludge

Figure 8 presents an inventory of the impact on agricultural soil of the sludge component from human dietary intakes, Swedish sludge concentrations and recommended maximum levels in sludge. The enhancement is in relation to the normal elements concentration in European soil (see section 2.3.1 for details). The black horizontal bar represents a doubling of the normal soil element concentration due to the sludge amendment; this is the very ambitious semi-voluntary Swedish target set to enable sludge amendment of agricultural soils over the next 500 years (Svenskt Vatten 2018; for two elements in figure 8, pragmatic levels have had to deviate from the ambition: zinc twice the ambition, copper 4 times). Note that the assumption of no leakage in 500 year leads to an overestimate of the impact since residence times in soil typically are less than a century (Bengtsson 2015). The following are some observations based on figure 8.

Diet. Even non-contaminated sludge may give more than a doubling of normal elements concentrations in topsoil for Ru, Rh, and Au, and all represented elements may give dietary contributions above 17 %. For several of the elements, the soil concentrations are very low and poorly known, so the data are uncertain.

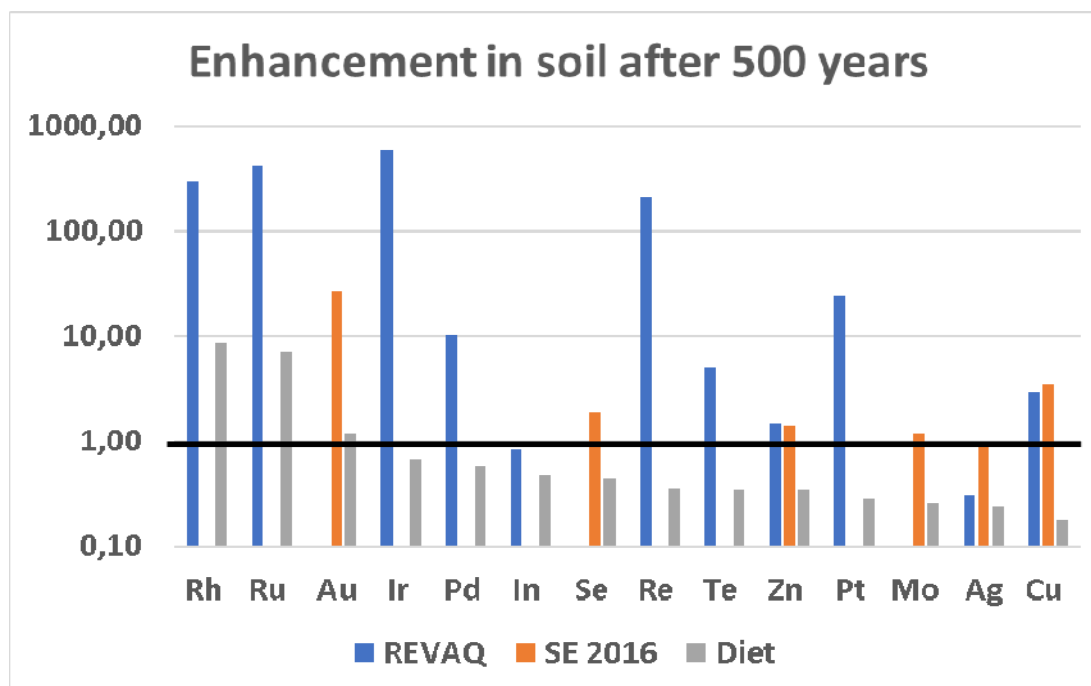


Figure 8. Calculated element enhancement in topsoil after 500 years of annual amendment with sewage sludge at an annual rate of 1 Mg/hectare, assuming no leakage from the topsoil. The 14 elements with the highest enhancements are ordered according to the enhancement of the dietary component. The ordinate scale is logarithmic.

The cases of sludge concentrations on which the diagram is based are:

- REVAQ: Recommended maximum concentrations in sludge in 2025 for a voluntary certification program for Swedish sewage sludge installations (Svenskt Vatten 2018)
- SE 2016: Average sludge concentrations in 2016 for 41 sewage treatment installations participating in the certification program (Anders Finnson personal communication 2017)
- Diet: Assumed sludge concentration if the sludge only would contain elements from human dietary intakes (section 3.1).

SE 2016. The sludge from certified Swedish sewage treatment installations in 2016 should represent very low element concentrations compared with those from most other countries. Still, following amendment more than a doubling of normal soil concentrations might be found for average levels of Au, Se, Zn, Mo, and Cu. Further, no concentrations were detected for Ru, Rh, Ir, Pd, In, Re, Te and Pt. However, Ru, Rh, Ir, and Re might well have non-detected concentrations corresponding to much more than a doubling. Indeed, the German study (Krüger and Adam 2014) included limited analyses of Rh, Pd and Pt and these had average element contents corresponding to 0.2 times, 2.8 times and 8 times the used Swedish limits of detection.

REVAQ. The certification levels might entail more than a doubling for Ru, Rh, Ir, Pd, Te, Re, Pt, and Cu. Further analysis would be needed to review if these levels should be revised, not the least in the light of the recent re-evaluation of platinum group element natural levels (Park *et al.* 2012).

An order of magnitude estimate of the impact of German sludge amendment in the years 1960-2011 can be obtained by assuming that the historical sludge concentrations have followed the average Swedish trend reported by Kirchmann *et al.* (2017) for 6 elements (section 2.4.1). By this estimate, the soil concentration of 7 elements would be more than doubled (P, S, Cu, Zn, Mo, Ag, Sb) if the same soil had been subject to annual amendment using 1 Mg/hectare.

3.3.4 Extrapolation to other elements in sludge

Figure 7 shows relatively small differences between calculated and measured element concentrations in German sludge. This encourages extrapolation of the calculation to elements that were not measured. The result of such an extrapolation is given in figure 9. The diagram is based on applying equation 2 with the parameter values found in producing figure 7. In figure 7, the calculated element concentration at most overestimates the measured concentration by a factor of 3 for all elements. It is thus unlikely that the true enhancements are less than one-third of those given in figure 9. Indeed, Rh, Pd and Pt were measured for a few samples in the German study. Their mean concentrations corresponded to 0.39, 0.51 and 2.3 of the calculated concentrations, respectively. These few measurements were thus within a factor of 3 of the estimated concentration, as concluded on the basis of figure 7.

Figure 9 shows that current German sludge element concentrations for the not measured elements are likely to exceed the unavoidable component from human dietary intake considerably less than for the 13 elements shown in figure 6. This is explained by the very high dietary intakes in relation to soil concentrations for most of these elements, as can be seen in figure 2. If such sludge were used for soil amendment for 500 years, with no element loss from the topsoil, it is however likely that the average element concentration in the soil would be significantly enhanced (by more than 5 %) for all elements listed in the diagram. More than a doubling is predicted for Re, Rh, Ru, Pd, Pt and Ir. Further research is warranted to find out if these predictions hold for closer scrutiny.

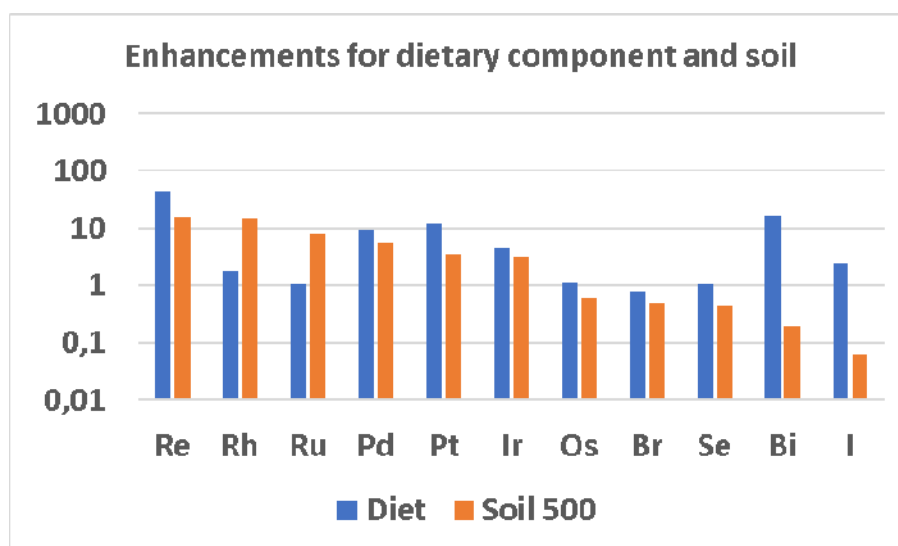


Figure 9. Calculated enhancements if equation 2 were valid for elements that were not measured in the German study (Krüger and Adam 2014). The parameter values found in deriving figure 7 have been applied. The left bar in each pair refers to the enhancement of element concentration in sewage sludge compared to that of the unavoidable dietary component. The right bar in each pair shows the enhancement in element concentration in soil that has been amended with 1 Mg/hectare of sewage sludge each year for 500 years, assuming no loss from the soil. The elements are ordered according to the extent of the soil enhancement. The diagram does not include elements that were deselected (section 2.4.2) or had both a dietary enhancement below 1 and a soil enhancement below 0.1.

3.3.5 Potential future enhancements of elements in sludge

Sludge levels have decreased strongly in the long term, not the least in Sweden. For instance, in Stockholm county, the concentrations of silver, chromium, and lead were reduced to one-fourth between 1981 and 2003 (Länsstyrelsen i Stockholms län 2014). At the national level, they were further reduced in 2016 (Anders Finnson personal communication 2017) to 0.2, 0.7, and 0.3, respectively, of the concentrations in 2000 (Eriksson 2001); the data sets are not strictly comparable, but the trend is clear. This trend may not continue in the long run. Indeed, the mean concentration over 68 elements was the same in 2016 as in 2000; the reduction to less than one-half for 17 elements was offset by more than a doubling for Be, Bi, Ga, Pt, and Se. There are several difficulties to be addressed for a more complete control of sludge levels even in Sweden with its very ambitious restrictions:

- There is no production monitoring of five potentially important elements (titanium, osmium, molybdenum, platinum and iridium).
- The semi-voluntary targets do not include the elements boron, cobalt, selenium, molybdenum, osmium, gold, and bismuth, among others. Gold occurred in Swedish sludge in the year 2000 at about 50 times the Swedish target levels, had they been stated by the same principle as other levels (23 of 25 soils had gold concentrations below the detection limit 0.005 mg/kg according to Eriksson 2001; the earth's crust

has a concentration of 0.0015 mg/kg). The not included element iron occurred in sludge at 343 times the level due to dietary intakes (based on Eriksson 2001).

- For a handful of elements, already their dietary component in sludge may entail more than a doubling of the natural levels in sludge amended soil, as exemplified in figure 8.
- There may be a strong link between global production of elements and sludge levels as suggested by the German data in figure 7. The global production for most elements is approximately doubling every 20 years. Even though European air emissions have been reduced over the last decades (section 2.2.3), produced elements may reach the sludge via other routes than air emissions (compare section 3.3.2) and these routes may be linked with production volumes.

The most likely scenario for the future may be a scattered development where concentrations in sludge for some elements may continue to decrease while those for other less abundant elements may be very difficult to restrict.

3.4 Environmental effects of enhanced element levels

The introductory question to this review was: Is a million-fold enhancement of natural element mobilisation a problem? While an exhaustive treatment of health and environmental effects is beyond the scope of this review, a few remarks on environmental effects will be made.

3.4.1 Is the mean rhodium concentration in topsoil already five-fold enhanced?

The quoted UNEP report (2013) mentions 5 non-gaseous elements for which the anthropogenic mobilization exceeds the natural one by more than 10 000 times: Re, Os, Ir, Pt, and Au. Those are the neighbouring elements 75-79 of period 6 of the periodic system. The corresponding elements in period 5: Ru, Rh, and Pd, have mobilisations in the range 50-6000 times.

In section 3.3.3 it was mentioned that the soil concentration of 7 elements (P, S, Cu, Zn, Mo, Ag, Sb) might have been more than doubled if the same soil had been subject to annual sludge amendment in the period 1960-2011 using 1 Mg/hectare. Using a similar calculation, figure 9 suggests that the same amendment might already have entailed multiplied soil concentrations of Ru, Rh, Pd, Re and possibly Pt and Ir, with Rh having the largest enhancement at about 5 times the natural concentration. The latter 6 elements can all be found among the highly mobilized elements in the previous paragraph. The former 7 elements have mobilisations below 50 times the natural ones. There is thus no clear relation between degree of mobilisation and risks from sludge amendment but obviously there is a correlation between extremely high mobilisation and risks to the topsoil from sludge amendment. To a large extent this risk relates to the legacy of very high earlier sludge concentrations with a cumulative load corresponding to 100-500 times the concentration in

the year 2012. If German sludge concentrations were decreasing in the future at similar rates as Swedish concentrations have, an additional doubling could be avoided, particularly since the element residence time in the soil is likely to be below a century. The backside of this relief is a concomitant threat to groundwater. The significance of such a shift is discussed by Bengtsson 2015.

What would the implications be of multiplied element concentrations in the topsoil? Soils have a wide distribution of element concentrations. The 90th percentile level is typically 1.6-2.0 times the mean concentration, and the maximum among the about 800 samples is often up to 10 times the mean (FOREGS 2005). Annual element deposition data have been obtained among about 60 monitoring stations across Europe (Torseth *et al.* 2012). These follow similar lines with a maximum up to about 10 times the mean. In limited locations, one would thus expect to find topsoils concentrations exceeding twenty times the the subsoil element content.

3.4.2 Will organisms be affected by topsoil element increases?

Organisms tend to be adapted to the environment in which they live. For fresh water organisms, for instance, no environmental effects should be expected in cases of compliance with Swedish reference levels where the concentration is 5–23 times the median natural concentration (Bengtsson 2015). Several pieces of evidence support the notion that harmful effects will only occur above the natural background levels.

For instance, extensive long-term field trials were performed in the United Kingdom (UK Water Industry Research Limited, 2007). The purpose was to see if metals in amended soil would disturb microbial life. The lowest observed adverse effect levels were near statutory limits for soil amendment in the United Kingdom. For cadmium, copper and zinc it translates to 11, 8 and 4 times the respective median natural metal levels in European soil of 0.15, 13, and 52 mg/kg (FOREGS 2005), a range of 360 times between highest and lowest.

The effects of a ten-fold enhancement of soil concentrations of platinum group elements in not known since few if any long-term low-level studies have been published (Sures *et al.* 2015). The example of gold may serve to illustrate that effects may be significant. Gold has been considered of low toxicity but effect levels of gold nanoparticles for aquatic organisms cover a similar range as those for silver (Moreno-Garrido *et.al.* 2015). Ionic gold further appears to be considerably more toxic than gold nanoparticles (Botha *et.al.* 2015). One silver compound (silver zinc zeolite) has a harmonized classification as very toxic to aquatic organisms (European Commission 2017), It cannot for the time being be excluded that a tenfold enhancement of platinum group elements in soil may have effects on microorganisms and other forms of life in soil.

In addition, most studies of environmental effects pertain to one element at a time and do not give information of the combined effect of many elements (Cedergren 2014). Within UNECE (2018), extensive efforts have been made to illustrate effects of pollution in Europe and North America. The research has been concentrated on air pollution and complex exposures such as

those from particulate matters and acidifying substances. A recent report (NIVA 2016) documents complex dependencies of defoliation and nutrient status of main tree species on concentrations of elements such as phosphorus, sulfur, and nitrogen. It also demonstrates recovery of aquatic species correlated with decreases in sulphate in deposition and associated increases in pH. For a few metals (lead, cadmium, and mercury), significant reductions of depositions of 15 % to 80 % are shown for the period 1990-2012. Soil concentrations of these elements mainly show an increase between 1994 and 2011, with much variation including reductions at many sites. Moss samples demonstrate similar reductions as for lead, cadmium, and mercury depositions for some more elements (As, Cr, Cu, I, V, and Zn). For the three metals Pb, Cd and Hg, areas with exceedance of critical loads have been mapped. The extent of these areas has in general been strongly reduced between 1990 and 2010. While such information is very illustrative, it has several weaknesses:

- it only pertains to a few elements
- definition of system limits will depend on the purpose of the assessment– should it for instance include cadmium input from agricultural activities or not?
- definition of the limiting values for critical loads requires decisions on a number of issues, highlighted in bold italic in the definition below; as an example of the complexity, the associated manual for mapping critical loads for ecosystems comprises 115 pages

Definition of critical load: “A quantitative estimate of an exposure to ***one or more*** pollutants below which ***significant harmful*** effects on ***specified sensitive*** elements of the environment ***do not occur***, according to ***present knowledge***.” (ICP 2018).

Lacking experimental information on the effects of the elements with the potentially highest enhancements in European soil (sections 3.2.2 and 3.3.3), extrapolations were performed on the basis of established thresholds for environmental effects (section 2.5). The results are given in Figure 10.

It is likely that the highest exposures of topsoils to elements will entail ecosystem and health effects but providing meaningful quantification is extremely complex or even impossible. Rather than defining unacceptable levels, decision makers have recognized that many times higher levels than the typical or median background levels are tolerable. Several examples of regulatory applications based on accepting element levels in addition to the natural ones are given by Bengtsson 2015.

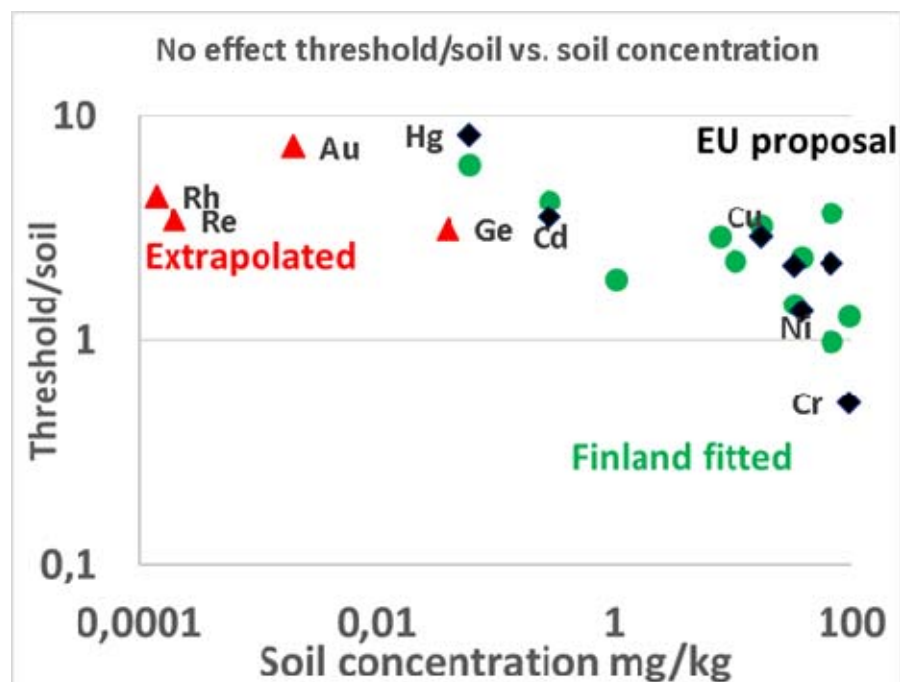


Figure 10. Thresholds for effects on soil organisms divided by mean European soil concentrations versus mean European soil concentrations. Black rhombs are from a proposed set of element thresholds for pH 6-7 (JRC 2006). Green circles represent a fitting of a set of element thresholds from the Ministry of the Environment, Finland (2007) to power functions of soil element concentrations and geometric mean of the elements' first three ionization energies. Red triangles are extrapolations to other elements using the function derived for the Finnish thresholds.

4. Conclusions

Human intakes of naturally occurring elements are conveyed to human excreta, which form a basic part of sewage sludge. The unavoidable element concentrations in sludge from excreta depend on natural element levels in the earth's crust. The transfer from soil solution via plants to humans depends strongly on chemical properties of the elements. The average daily intakes in human diets can for most elements be predicted within a factor of 3. This prediction might be refined through further research concerning relevant chemical parameters.

The dietary contributions to sludge element concentrations have been enhanced by human activities employing elements extracted from the earth's crust. Element concentrations in **sewage sludge** are often enhanced beyond the inevitable contributions from human excreta. Contributions due to collateral emissions from fossil fuel burning have been curtailed in recent decades but still dominate for elements with low global production volumes. For instance, in the German case (Krüger and Adam 2014), the 12 elements with the lowest global production volumes (Sc, Ho, Lu, Tm, Yb, Tb, Ge, Eu, Th, Ga, Er, Dy) all had an estimated coal fraction above 0.91 of the mobilized mass. Despite significant efforts for upstream reduction, average Swedish sewage sludge levels in 2016 may be enhanced a hundredfold or more for 8

elements (U, Bi, Ti, Sc, Y, Th, Ga, Pb, Zr). The highest enhancement refers to uranium at 340 times the diet-related level. Estimates based on German sludge data suggest that platinum group element concentrations would not rank among those with the highest enhancements. Two factors might explain this:

1. the enhancement is indeed low, since these elements have extremely high normal dietary intakes which include several of the highest transfer factors between soil and diet (figure 2).
2. the enhancement may be artificially low, since the dietary intakes might be strongly influenced by existing contamination of agricultural soils; if the normal dietary intakes were several times lower than measured ones, then the ratio sludge/diet would be several times enhanced.

In European **topsoil**, the average concentration of 19 elements may have been measurably increased. These elements may include the 8 platinum group elements (Ru, Rh, Pd, Re, Os, Ir, Pt, Au) for which very few measurements are available.

Human consumption of elements is likely to be more than doubled over the next generation. The strong emission reductions in recent decades are likely to entail limited additions to topsoil element concentrations over the next generation. Sludge concentrations may come to exhibit a scattered picture with significant reductions for some elements and large increases for others.

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Used terms

Diet/soil: The mean dietary intake of an element over large population groups divided by the mean concentration of the corresponding element in the topsoil

Mobilised element mass: sum of the mass of elements consumed and the mass of the same element contained in the consumed mass of coal

Emitted fraction: mass of an element emitted to air in a region divided by the mass of this element in the combusted fuel or in the mass of element from production, fabrication and use in this region.

FOREGS countries: countries participating in the soil mapping of FOREGS (2005): Austria, Albania, Belgium, Croatia, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, The Netherlands, Norway, Poland, Portugal, Slovak Republic, Slovenia, Spain, Sweden, Switzerland, United Kingdom.

Appendix. Dietary intakes of elements

The table gives the selected dietary intakes over large population groups as an average for male and female adults. The dietary intake divided by the soil element concentration is also given (diet/soil).

The entry *Selected* in the table is a selected intake based on the considerations in the text in section 2.1. The *Data sources* heading gives a list of one or more mean daily intakes in $\mu\text{g}/\text{day}$ with a superscript that leads to the respective literature reference. The reference Parr *et al.* (1992) is a compilation of many dietary intake studies. The sources for the lanthanides and scandium are discussed in section 2.1.7. For the other elements, the main literature references are given by the superscripts.

Elem.	At. No	Selected □g/d	Data sources
Li	3	50	48,2 ^{ANS} ; 54 ^{Gim} ; 28,5 ^{INR} ; 300 ^{Kab} ; 50 ^{Par} ;
Be	4	3	0,14 ^{HCa} ; 30 ^{Kab} ; 0,5 ^{W18} ;
B	5	1400	1500 ^{FEH} ; 1200 ^{W18} ;
C	6	16000000	12000000 ^{Alm} ; 16000000 ^{R15} ;
Na	11	3000000	3180000 ^{Alm} ; 2650000 ^{ANS} ; 3635000 ^{Erv} ; 2600000 ^{FEH} ; 2300000 ^{INR} ; 2900000 ^{Max} ; 3500000 ^{W18} ;
Mg	12	300000	305000 ^{Alm} ; 304000 ^{ANS} ; 295000 ^{Erv} ; 210000 ^{FEH} ; 224000 ^{INR} ; 413000 ^{Max} ;
Al	13	3000	2820 ^{ANS} ; 6000 ^{FEH} ; 2700 ^{FSA} ; 5470 ^{Gar} ; 8700 ^{HCa} ; 1620 ^{INR} ; 4970 ^{R10} ;
Si	14	28000	28400 ^{Ins} ; 28000 ^{Jug} ;
P	15	1200000	1380000 ^{Alm} ; 1363000 ^{Erv} ; 1000000 ^{FEH} ; 1200000 ^{Wün} ;
S	16	700000	849000 ^{Alm} ; Rose 658000
K	19	2900000	3010000 ^{Alm} ; 2820000 ^{Erv} ; 1900000 ^{FEH} ; 350000 ^{Max} ; 2920000 ^{W18} ;
Ca	20	800000	968000 ^{Alm} ; 881000 ^{Erv} ; 430000 ^{FEH} ; 721000 ^{INR} ; 1081000 ^{Max} ;
Sc	21	0,35	0,35 ^{Par} ;
Ti	22	300	300 ^{Kab} ; 4156 ^{Wün} ; 350 ^{W18} ;
V	23	15	60,4 ^{ANS} ; 15 ^{Eo4} ; 15 ^{Par} ;
Cr	24	50	140 ^{Alm} ; 110 ^{FSA} ; 70 ^{Gar} ; 76,9 ^{INR} ; 57,5 ^{Mar} ; 22,75 ^{R10} ; 147 ^{Wün} ;
Mn	25	3500	4300 ^{FEH} ; 2470 ^{Gar} ; 4100 ^{HCa} ; 2310 ^{INR} ; 2229 ^{Mar} ; 4690 ^{R10} ; 3500 ^{Wün} ;
Fe	26	10000	45000 ^{Alm} ; 15650 ^{Erv} ; 8000 ^{FEH} ; 13800 ^{Max} ; 9700 ^{Wün} ;
Co	27	10	12,6 ^{ANS} ; 9,4 ^{FEH} ; 12,6 ^{HCa} ; 7,53 ^{INR} ; 17 ^{Wün} ;
Ni	28	150	241 ^{Alm} ; 163 ^{ANS} ; 217 ^{FEH} ; 391 ^{Gar} ; 273 ^{HCa} ; 93,7 ^{INR} ; 78 ^{Mar} ; 109,2 ^{R10} ; 250 ^{Wün} ;
Cu	29	1300	1790 ^{Alm} ; 1300 ^{Erv} ; 920 ^{FEH} ; 1240 ^{Gar} ; 1382 ^{HCa} ; 980 ^{INR} ; 1206,1 ^{R10} ; 1200 ^{Wün} ;
Zn	30	10000	12150 ^{Erv} ; 9200 ^{FEH} ; 13940 ^{Gar} ; 12320 ^{HCa} ; 8660 ^{INR} ; 11900 ^{Max} ; 9849 ^{R10} ; 9800 ^{Wün} ;
Ga	31	3	0,502 ^{ANS} ; 2 ^{Kab} ; 21 ^{Wün} ;

Ge	32	2	4,28 ^{ANS} ; 8,85 ^{Gar} ; 2,9 ^{Gim} ; 0,315 ^{R10} ;
As	33	50	54,9 ^{ANS} ; 40 ^{FSA} ; 61 ^{HCa} ; 62,1 ^{INR} ; 351 ^{Mar} ; 40 ^{Par} ; 116,2 ^{R10} ;
Se	34	60	114 ^{Erv} ; 140 ^{FEH} ; 130 ^{FSA} ; 135 ^{Gar} ; 152 ^{HCa} ; 41,8 ^{INR} ; 60 ^{Par} ; 62,3 ^{R10} ;
Br	35	4000	4000 ^{Par} ;
Rb	37	2000	2682 ^{HCa} ; 1700 ^{Kab} ; 2400 ^{Wün} ;
Sr	38	1700	1650 ^{ANS} ; 1850 ^{FSA} ; 2004 ^{Gar} ; 2100 ^{Gim} ; 1553 ^{HCa} ; 1700 ^{Kab} ; 1092 ^{R10} ; 1400 ^{Wün} ;
Y	39	2	1 ^{Kab} ; 4,2 ^{Wün} ;
Zr	40	30	19 ^{Wün} ;
Nb	41	20	50 ^{Kab} ; 2,5 ^{Wün} ;
Mo	42	100	93,9 ^{ANS} ; 110 ^{FEH} ; 136 ^{Gar} ; 113,75 ^{R10} ; 110 ^{Wün} ;
Ru	44	0,30	0,14 ^{R10} ; 1,1 ^{Wün} ;
Rh	45	0,50	0,3 ^{Kab} ; 0,7 ^{R10} ;
Pd	46	1,00	1 ^{Kab} ; 0,63 ^{R10} ;
Ag	47	30	33 ^{Alm} ; 129 ^{ANS} ; 4,3 ^{Wün} ;
Cd	48	10	15,9 ^{Alm} ; 11 ^{ANS} ; 14,7 ^{Bfr} ; 19,4 ^{FEH} ; 7 ^{FSA} ; 11,9 ^{HCa} ; 2,43 ^{INR} ; 4,6 ^{Mar} ; 10,85 ^{R10} ; 14 ^{Wün} ;
In	49	10	10 ^{Kab} ; 9,8 ^{R10} ;
Sn	50	300	570 ^{ANS} ; 300 ^{FEH} ; 37,9 ^{Mar} ; 1634,5 ^{R10} ;
Sb	51	2	2,34 ^{ANS} ; 1,925 ^{FEH} ; 9,62 ^{Gar} ; 1 ^{INR} ; 2,275 ^{R10} ; 3,5 ^{Wün} ;
Te	52	3	2,61 ^{ANS} ; 2,2 ^{Gim} ;
I	53	130	170 ^{Cha} ; 56 ^{Kab} ; 103 ^{Max} ; 166 ^{Wün} ;
Cs	55	10	10,4 ^{HCa} ; 10 ^{Kab} ; 10 ^{Par} ; 8 ^{Wün} ;
Ba	56	600	448 ^{ANS} ; 437 ^{Gar} ; 488 ^{HCa} ; 800 ^{Kab} ; 658 ^{R10} ; 718 ^{Wün} ;
La	57	8,1	7,4 ^{HCa} ; 2,5 ^{Wün} ;
Ce	58	10,6	4,5 ^{Wün} ;
Pr	59	1,9	

Nd	60	6,3	
Sm	62	1,1	
Eu	63	0,5	
Gd	64	1,1	
Tb	65	0,4	
Dy	66	1,0	
Ho	67	0,2	
Er	68	0,5	
Tm	69	0,1	
Yb	70	1,7	
Lu	71	0,1	
Hf	72	1,0	1 ^{Kab} ;
Ta	73	1,0	1 ^{Kab} ;
W	74	3,0	10 ^{Han} ; 1 ^{Kab} ;
Re	75	0,03	0,03 ^{Kab} ;
Os	76	0,03	
Ir	77	0,02	0,02 ^{Kab} ;
Pt	78	0,20	0,3 ^{Kab} ; 0,7 ^{R10} ; 1,4 ^{W18} ;
Au	79	1,0	1,05 ^{E16} ; 1 ^{Kab} ; 3,2 ^{Wün} ;
Hg	80	4	9 ^{Alm} ; 4,74 ^{ANS} ; 4,9 ^{Bfr} ; 7,4 ^{FEH} ; 7 ^{FSA} ; 9,65 ^{INR} ; 7,1 ^{Mar} ; 2,31 ^{R10} ;
Tl	81	2	1,2 ^{HCa} ; 2 ^{Kab} ; 0,805 ^{R10} ; 5 ^{W18} ;
Pb	82	10	37 ^{Alm} ; 14,1 ^{ANS} ; 37,1 ^{Bfr} ; 14,7 ^{FEH} ; 7 ^{FSA} ; 7,8 ^{HCa} ; 18,4 ^{INR} ; 39,9 ^{Mar} ; 6,65 ^{R10} ; 77 ^{Wün} ;
Bi	83	1,0	3,64 ^{Gar} ; 0,44 ^{HCa} ; 1,295 ^{R10} ; 0,7 ^{Wün} ;
Th	90	0,5	0,9 ^{Cha} ; 0,245 ^{FEH} ; 0,29 ^{HCa} ; 0,313 ^{R15} ;
U	92	2,0	1,82 ^{Cha} ; 5,46 ^{FEH} ; 6,1 ^{HCa} ; 0,258 ^{R15} ; 1,5 ^{Wün} ; 2,5 ^{W17}

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